A LABORATORY COMPARISON OF THE ADHESION OF UNFILLED AND COMPOSITE RESINS TO ACID ETCHED ENAMEL

by

Robert W. Aubuchon

Submitted to the Faculty of the Graduate School in partial fulfillment of the requirements for the degree of Master of Science in Dentistry, Indiana University School of Dentistry, 1973.

ACKNOWLEDGMENTS

For his guidance and concern during my graduate education, I am grateful to Dr. James R. Roche.

For his advice and counsel during my pedodontic education, a special thanks is given to Dr. Paul E. Starkey.

For her assistance and advice during this project, I wish to thank Professor Marjorie Swartz.

A special thanks goes to Professor Paul Barton for his editorial comments and to Mrs. Vivian Haggard for her expert typing.

I am especially grateful to my graduate committee which included Drs. Roche, Koerber, and Starkey, and Professors Swartz and Barton.

Thanks is offered to Mr. Richard Scott and his staff for compiling the photographic portions of this thesis.

In addition I am very grateful to Dr. Bernard Smith for his encouragement, advice and friendship during my academic career.

Finally the author wishes to thank his wife, Ginny, for her love, faith, and encouragement.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

TABLES

FIGURES

PAGE

INTRODUCTION

A major difficulty with every dental restorative material has been its lack of adhesion to tooth structure. Countless studies have shown this lack of adhesion and consequent marginal leakage.[90,92,96]

Lack of adhesion has profoundly influenced the theory and practice of dentistry today. Preparation design, removal of carious material, and methods of retaining appliances in the oral cavity are procedures that were developed to compensate for the lack of adhesion. If an adhesive material were to become available, not only would past principles of dentistry be changed, but new areas of prevention would become available.

In 1959 the National Dental Research Council designated the development of an adhesive restorative dental material as a top priority for dental research.[11] In the past few years great expense and effort have been devoted to the development of such a material. Some significant advancements have been made.

Developing a material that will bond to tooth structure is a complex problem because of the many factors which tend to inhibit bonding.[2-4] The chemical reactivity of the tooth is poor because of its heterogeneous composition and the relatively low reactivity of the organic and inorganic phases. Contaminants are present in the form of water and mechanical debris.[3-5] The contaminants as well as surface irregularities interfere with the dynamics of surface contact or wetting by the adhesive. Even when these problems can be overcome, the physical properties of the adhesive are significantly different from those of tooth structure and invariably the bond that is formed is loosened in time.[21,23,92]

These factors, combined with the fact that the oral environment has a wide range of temperature and pH changes, as well as extreme mechanical stress, would disrupt all but the most stable of bonds.

Probably each of the factors interfering with adhesion to a tooth should be investigated. However, to date there have been two basic areas of investigation: 1) Pretreating the tooth's surface with chemicals in an effort to enhance the bonding ability of the tooth; and 2) attempting to develop a restorative material with physical properties similar to those of tooth structure.

Surface pretreating agents can act in three major ways: they can physically alter the tooth's surface, they can remove surface contaminants, and they can form an intermediate coupling layer over the tooth. The enamel proteins have been removed by enzymes[18] or they can be made more hydrophobic by crosslinking.[18] Etching with acid has increased the surface area of the tooth by exposing more hydroxyapatite and at the same time removing surface debris.[7,27-28] Water contamination can be eliminated by water repellent agents.[6] Chemicals with a high affinity for tooth structure and for plastic restoratives have been used to line the cavity preparation and thus increase the adhesion between the tooth and the restorative material.[19] Sometimes these pretreatment agents have been used in combination.

Research in plastic chemistry is the second area in which attempts have been made to improve adhesion. Presently there are two popular types of plastic restorative materials: the poly (methylmethacrylate) resins and the composite or filled resins.[29]

The poly (methylmethacrylate) resins were originally developed as denture materials. Later they were modified for use as tooth restoratives. Improvements have been made on poly (methylmethacrylate) resins over the years, but unfortunately their physical properties do not approach those of tooth structure nor do they bond to either enamel or dentin. Efforts to improve the physical properties led to the development of the composite resins.

The physical properties of composite resins approach those of tooth structure.[48] Much of the recent adhesive research is devoted to determining whether surface pretreating agents that increase the bond strength between unfilled resins and tooth structure also will increase the bond strength between the tooth and composite resins.[99,101]

Of the many methods investigated for improving the bond strength between a plastic restorative and tooth structure, the acid etch technique seems most promising.[65] One of the first reports on the use of acid pretreatment of the enamel to strengthen the tooth-restorative bond was by Buonocore (1955).[66,67] Several later studies have demonstrated increased bond strength between unfilled resins and the acid etched tooth.[18,19,28,65,68-73]

There is little evidence concerning the effects of the acid etch technique on the retention of composite resin. However, there is indirect evidence that the technique should work well for both filled and unfilled resins. Sharpe and Grenoble[99] have shown that resin "tags" form on composite resins in the same way that they do on unfilled

resins when they are applied to an acid etched surface. Brauer and Termini[101] incorporated a few composite resins in a large study designed to determine the effectiveness of various acids on tooth adhesion. The results indicated that acid etching does increase the bond between enamel and composite resins. However, a more extensive study is needed in this area before any conclusions can be made concerning the degree of the increase in bond strength obtained through the use of the acid etch techniques.

The present investigation was undertaken to evaluate the effects of etching enamel surfaces on the bond strength of unfilled and composite resins.

REVIEW OF LITERATURE

This survey of the literature will deal with problems involved in tooth adhesion, methods of increasing adhesion to tooth structure, and the development of new resins systems. The acid etch technique of increasing tooth adhesion will be stressed in a separate section.

PROBLEMS INVOLVED IN ADHESION TO TOOTH STRUCTURE

For an appreciation of the difficulty of developing adhesives for tooth structure, it is important to understand the physics of adhesion and cohesion.[1] Cohesion occurs between molecules of the same material, whereas adhesion occurs between unlike molecules or materials. Both adhesion and cohesion occur through the molecular attraction of hydrogen bonding, ionic bonding, and Van Der Waals forces. However, only the cohesive bond can use the highly stable covalant bond. One major principle involved in either form of bond is that intimate contact between two principals must be formed to obtain a bond. This is due to the short distances through which these forces act. In adhesive chemistry the ability of one compound to form an intimate contact with another object or to "wet" the surface of the substrate is of prime importance in evaluating the potential adhesiveness of the material.

The development of a material that will bond to tooth structure is a complex problem because of the many factors which tend to inhibit bonding.[2-4] Tooth structure is heterogeneous in composition. Both the enamel and dentin consist of an inorganic component in the form of hydroxyapatite and an organic component of protein; these entities are chemically different and react differently with any given substance.

Thus it is difficult to find a compound that bonds chemically to all phases. This is further complicated by the fact that the composition of enamel and dentin differ with respect to the percentage of organic and inorganic components. A major factor that interferes with adhesion to the tooth is water contamination.[3,5] In fact, the best that can be achieved is to remove all but a monomolecular surface layer of water from a prepared tooth's surface.[6] This water layer prevents intimate contact between the tooth and the adhesive. Another factor contributing to low bond strengths is the presence of debris on the prepared tooth surface. Debris interferes with the spreading or "wetting" of the tooth's surface and decreases the homogeneity of that surface. Temperature fluctuation may result in loss of adhesion because of differences in thermal expansion between the adhesive and tooth structure. When such a material is placed on the rough surface of a tooth, temperature fluctuation produces stress concentrations around each irregularity in the surface. In an article on stress in dental materials, Mahler[8] stated: "Any discontinuity such as a hole or notch can disrupt an otherwise uniform stress picture and produce a very high stress within the vicinity of the discontinuity."

Stress concentrations also are created when total adhesion does not occur. Pinpoint areas where the adhesive is not bonded will act as foci for stress. These stress concentrations can eventually weaken the bond and separate the adhesive from the tooth. This phenomonon has been described by Erich,[9] who said, "If thermal and mechanical stresses at the interface exceed the adhesive bond strength and create voids by

dewetting, these voids will not only interfere with stress transmission but lead to stress concentrations with consequent crack propagation or further dewetting."

The roughened surface of the tooth further complicates the ability of the adhesive to bond by decreasing the wetability of the tooth's surface. Since small voids at the depth of the roughened areas remain uncovered by adhesive, this again contributes to stress concentrations.[10] The dental adhesive must maintain its bond in the unfavorable environment of the oral cavity. These bonds are constantly subjected to the forces of mastication and bathed in oral fluids that vary in temperature, acidity, and chemical composition.

METHODS OF INCREASING ADHESION TO TOOTH STRUCTURE

Each of the above factors interfering with the adhesion to tooth structure should be investigated in order to develop a truly adhesive bond. However, because the problem of tooth adhesion is complex, no one person or discipline can be thoroughly acquainted with the latest theories and developments in each related area. This fact, and the further fact that a truly adhesive restorative material would raise current dental procedures to a status approaching the ideal, have led the national advisory dental research council to assign this area as a "top priority" in dental research.[11] In 1959 council appointed a preliminary planning committee with the specific purpose of concentrating attention on this area. In 1960 a dental adhesive workshop was organized and implemented to investigate the problems of dental adhesion.

Participants in this workshop had backgrounds in surface chemistry, polymer chemistry, adhesive science, and dental materials. R. W. Phillips,[11] chairman of that meeting, pointed out that it was the first time that an interdisciplinary approach of this type had been brought to bear upon a dental problem.

After what was considered a successful meeting, an ad hoc advisory committee was formed to help implement the suggestions presented at the 1960 workshop. The committee kept abreast of current research and helped to direct further research in dental adhesives. This helped prevent duplication of effort. At a second workshop in 1965, new areas were discussed and progress reports were made.

Research into adhesives ranges from remotely related studies to those which deal with prospective dental materials or adhesion to tooth structure. Research in surface chemistry has led to new methods of determining isotherms for chemicals that are absorbed on to the tooth's surface.[12] These were adapted in subsequent studies to screen chemicals for use as adhesive liners.[13,14] Extensive efforts have been made to grow pure crystals of hydroxyapatite for use as a "model substrate."[15] Theories on the mechanism and thermodynamics of surface wetting proved helpful in understanding adhesion. The elucidation of the chemical composition of enamel and dentin[16] and the lattice structures is also related.[17] Further studies investigated the chemical nature of the organic component of tooth structure, while others investigated the microstructure of the tooth surface when cut by dental instruments.[7] Each of these areas is related to adhesion and represents an interdisciplinary approach to the development of a dental adhesive.

In general, two research approaches have evolved: (1) one approach in which the tooth's surface is pretreated to enhance its susceptibility to adhesion, and (2) another approach which involves synthesizing materials that have physical properties acceptable for a dental restorative.

Increasing Adhesion by Surface Treatment

Many surface treating agents have been used, some of them in combination. Moisture has been a major problem in developing adhesion to tooth structure. A number of approaches to circumvent this problem have been investigated. Elemination of the water has been attempted by means of chemicals that push the water molecules out of the way, leaving the tooth coated with a film of water repellent agent.

Zisman[6] experimented with various chemicals with respect to their displacing properties. Butanol removed all but a monomolecular layer of water from the surface of a glass plate. Perfluoroalkanols and dimethylsilicones were most effective in removing organic chemicals, but each liquid contaminant had an optimum displacing solvent which was dependent upon the physical properties of the liquids. In general, the displacing agent must have a lower surface tension than the liquid being displaced and a low solubility in the displaced substrate. When this relationship exists, the displacing liquid spreads violently over the surface of the substrate carrying the substrate back via surface drag.

Another approach to the elimination of water from the interference of bond formation is to make the dental protein layer more hydrophobic. Thus it can not act as a water conductor and disrupt the tooth restoration bond.

Lee[18] reasoned that because dentin contains an organic component which is 18% by weight and 39% by volume, this very hydrophilic material was constantly feeding water to the bond interface. He and his associates attempted to cross link the collagen fibrils in dentin, making it more hydrophobic. They used zirconium as a cross linking agent. In preliminary studies on collagen in an effort to determine the optimum conditions in which cross linkage would occur, they found that zirconium acetate was an effective cross linking agent at the proper pH.

A third approach to overcoming the moisture problem is to incorporate it into the bond of the restoration. Theoretically if the water is incorporated into the chemical reaction of bonding, it would in effect be removing the water from the surface of the tooth.

Munia, Nakagaiva, and Masuhara[19] investigated a new resin system for its potential adhesion to enamel. This methyl methacrylate acrylic has a catalyst of tri-n-butyl borane which will initiate the polymerimation reaction upon contact with the water present on the surface of the tooth. Thus the surface contaminant is involved in the bond formation.

Invariably, however, researchers have reported loss of adhesive properties once the adhesive came in contact with water.[20,21,24] The phrase "surface active comonomer"[22] was developed for a compound that, after coating a tooth's surface, would make the tooth more reactive to the adhesive and less reactive to H_2o; or to put it another way, the tooth would become less hydrophilic and more organophilic. Eastman marketed such an agent called Eastman 910. It was basically a cyanoacylate consisting of n-phenylglycine and glycidyl methacrylate

(NPG-GMA). Although surfaces treated with this material were still susceptible to water contamination, there was a marked improvement in adhesive qualities.[22-24]

The hydroxyapatite surface can be made more reactive by coating its surface with a coupling agent. This agent would react with the surface of the tooth and also with the restorative material, thus coupling them.[13,20,25]

Silane primers became popular as coupling agents for dental restoratives as a result of the extensive work by Bowen in developing the composite resins. Lee[18] stated:

> The rationale for the use of silanes in dentistry is based on industrial fabrication of glass reinforced epoxy resins in which it was found that silane treatment not only increased adhesion of the epoxy polymer to the glass substrate but also resulted in marked retention of strength when specimens were exposed to water. Laminates without silane treatment retain their strength for only one year in hot water, whereas, based upon accelerated tests silane-treated laminates retain their strength for 50 years.

Lee added that "Silane can and does increase adhesion to dentin when the surfaces are properly treated."

The use of several different chemicals has been suggested to increase the reactivity of the tooth structure. In a typical system one chemical would first be used to displace the water from the surface of the tooth. Another chemical could then be used to cover the hydroxyapatite crystal and increase its reactivity. Then a "rubbery" intermediate could be placed over the primer followed by the adhesive resin restorative. The rubbery layer would act as an expansion joint by adjusting to slight differences in thermal expansion between the tooth

and the resin. This intermediate layer would also smooth the rough surface of the tooth. In both cases the result would be to decrease stress concentrations.

Patrick, Kaplan, and Beaver[26] studied such a laminated system. They used isotherm absorption studies to select chemical compounds that would be the most reactive with tooth structure. They chose polyacrylonitrilebutyl acrylate as the rubbery intermediate and silane as the initial primer. A punch shear test was used to determine adhesion of this system and it was compared to an untreated tooth. The control tooth had adhesion values of 3,415 $\pm$ 198 psi and the laminated system yielded values of 4,610 $\pm$ 290 psi. To check the effect of water on the bond, adhesion under water was examined as a function of time. Total adhesion in both systems was reduced by contact with moisture. The laminate system decreased to 4,100 psi and remained at this strength whereas the control dropped to 1,000 psi before leveling off.

The elimination of debris from tooth preparations was studied by Provenza and Sardana.[7] They used electron and optical microscopes to study the surface of enamel and dentin prepared with dental instruments. Colloidan replicas were obtained of the cavity walls. The colloidan solution was painted in a thin layer on the walls, then stripped away and photomicrographed. Debris was present on both the enamel and dentin surface. To determine the relative ease with which this debris could be removed, the surfaces were treated with detergents, hydrogen peroxide, O.IN hydrocloric acid, ethylenediamine, and anti-static brushing. None of these procedures completely removed the debris.

It was proposed that the debris might have been packed into the tubular holes too deep for removal by conventional methods.

Efforts have also been made to increase the homogeneity of the tooth surface so that a more uniform bond would be obtained. Enzymes have been used to remove the organic phase of the tooth structure, thereby exposing more hydroxyapatite to participate in the bonding mechanism.

Lee[18] used bovine pancreatic trypsin and collagenase to remove the organic material from the surface of teeth. To check effectiveness, he used photomicrographs of bovine enamel and dentin before and after treatment with the enzymes. He had observed a lack of definition of the tubules and the presence of debris on the surface in the untreated samples. After treatment with the enzymes, the tubules were well defined.

Probably the most successful method of pretreatment involves increasing the surface energy of the tooth, thereby making them more wettable. Acid has performed this function very well and at the same time has increased the total surface area. Acid treated enamel has proved easier to wet,[28] and other studies have shown increased bond strength between the resin and enamel.[27] The literature concerned with etching of the enamel surface will be further discussed later in this review.

Increasing Adhesion Through Improved Restoratives

In recent years attempts to develop a restorative material that adheres to tooth structure have been mainly in the area of plastics.

Hydrocarbons offer a wide range of chemical and physical properties. Because of the versatility of these compounds and the knowledge that has been accumulated in plastics and polymeric chemistry, it is not surprising for research to be concentrated in this area.

When selecting a plastic as a dental restorative material, two considerations are of major importance:[20] (1) The unpolymerized monomer must be a liquid at 37°C, and (2) the monomer should polymerize or harden in about 3-8 minutes at this temperature. The restrictions greatly limit the number of suitable plastics. According to Lee,[20] of about fifty plastics in existence today, all but seven types fail to meet these qualifications. Polymethylmethacrylate, polystyrenes, allylic resins, epoxy resins, polyurethane, thermosetting acrylics, and unsaturated polyesters are the major plastic groups that can be considered for dental restorations.

The next most important consideration for a suitable plastic system is the rate or speed with which these chemicals will react to form the product. However, this is not a limiting consideration as chemists have learned to control the rate of a reaction with catalyst or by other modifications. Methylmethacrylate has an appropriate reaction rate at 37°c. This material has been used in dentistry for many years.

The methylmethacrylate system has certain shortcomings with respect to physical properties.

It has a low hardness number, low tensile and compressive strengths, low yield strength, and a low modulus of elasticity.[29] Low values for

both yield strengths and modules of elasticity indicate that plastic flow and deformation of the restorative are more likely to occur. The hardness of a material, on the other hand, gives a general indication of its resistance to wear and to the overall properties of the material.

Probably the most difficult problem with the poly (methylmethacrylate) system has been polymerization shrinkage.[30] This problem has been partially eliminated by manipulative techniques.[29,30]

Schouboe, Paffenbarger, and Sweeny[21] examined several acrylic resins in 1956 and found that they had a polymerization shrinkage of 3.4 to 8.3%. None of them would adhere to ground enamel after storage in water.

Phillips[31] in 1955 stated: "Failures with theself-cured resins in restorative dentistry generally can be associated with known inherent shortcomings in the physical properties of the material." He said that improvements were being made by improving the color stability and developing new techniques of application to reduce polymerization shrinkage.

Seltzer[32] used bacteria to study two techniques of placing acrylic restorations. He used what is called the bulk pack technique in which the acrylic is placed in the preparation in total and held under pressure, and the bead-flow technique, in which small increments are placed in the preparation. Theoretically the bead-flow technique was developed to reduce the polymerization shrinkage by having each successive addition of acrylic refill the partial shrinkage of the increment just ahead of it. Seltzer concluded that there was no difference in the techniques employed; Restorations placed by both techniques demonstrated marginal leakage.

This finding was in conflict with the results of Sansen, Armstrong, and Simon.[33] They used calcium[45] and found leakage in restorations placed with both techniques, but more leakage was found with the bulk pack technique. This view is commonly accepted.

Masuhara, Tarumi, and Nadabayashi[34] experimented with trialkylborons as initiators of poly (methylmethacrylate) selfcuring resins. Curing times for these resins varied from 8 to 60 minutes and were considered inappropriate for dental use.

Other systems have been evaluated as possible substitutes for the poly (methylmethacrylate) systems.

The epoxy resins have several desirable characteristics which set them apart from the others. In industry they develop strong and permanent adhesive bonds at atmospheric pressure, they have low polymerization shrinkage, and the cured polymer demonstrates desirable qualities of abrasion resistance, toughness, and hardness.[20]

The epoxy gets its name from a three-membered cyclic ether ring. This ring is the reactive group and is responsible for the chemical reaction leading to the polymerization. Although the reaction products are still referred to as an epoxy resin, they no longer contain the three-membered cylic ring. One advantage of this system is that the hydrocarbons attached to this cylic ether ring can be varied to produce more desirable physical properties of the epoxy resin. Bowen[35] found that a combination of epoxy and methylmethacrylate was a good prospect for a dental restorative material. This type of resin can be characterized as a molecule which contains the methacrylate groups on the

ends of an interconnecting hybrid epoxide molecule. This large hybrid molecule could undergo other chemical reactions, which enabled Bowen and other workers to increase its desirable physical properties. Other compounds were investigated as possible dental restoratives, including isocyanoates, cyanoacrylates, and marine secretions.

Bernstein[23] in 1965 used a cyanoacrylate marketed by the Eastman Corporation to cement orthodontic brackets on teeth. This material, commercially known as Eastman 910, was found to lose adhesion to the enamel surface after contact with water. Bernstein was able to increase the bonding strength, however, when he made brackets that could be cemented to the tooth's surface with a thin film of adhesive. In one case adhesion remained after forty days in an aqueous environment.

Khowassah and Sahs[36] in 1966 examined the adhesive properties of the same Eastman product. Based upon their study of marginal sealing ability, they labeled this cyanoacrylate as a promising dental adhesive.

In 1967 Blair[37] examined three plastic systems for adhesive properties. Using a modified peal test of metal-to-metal adhesion and acrylic-to-metal adhesion, it was determined that the cyanocrylate was better than either the epoxy or the polyester.

An extensive investigation on the possible use of isocyantes or polyurathens was undertaken by Buonocore[39] in 1969. Prior to this he had become interested in the possibility that these polymers could theoretically react with the proteins of tooth structure and thus would lead to covalent bonding and a more adhesive material. Foaming and other unsuitable physical properties precluded their use. However,

because the polyisocyanate prepolymers had such a variety of reactions, he still considered them an ideal system for a dental restorative. Other approaches were used, and a polymer was synthesized that showed less marginal leakage than any other material that he or his associates had encountered. This resin, however, showed a great amount of water sorption and still needed further refinement. This softening by water sorption was thought to be correctable by Buonocore and he concluded that the resin showed much promise.

In 1970 Lee and Swartz[39] reported an in vitro study of a prospective pit and fissure sealant made from a urethane prepolymer. It gave an initial adhesive strength of 1300 psi. After one year of storage in water it had lost only 10 percent of its bond strength. Autoradiographs and a scanning electron microscope were used to determine that no leakage had occurred during that time.

Bioadhesives such as those secreted by barnacles, oysters, star fish, sea urchins, and sea cucumbers have also interested researchers. These adhesives have the unique ability to form and maintain an adhesive bond in the presence of H_2O, and to adhere to a variety of substances.

Cardilli[40] submitted a report in 1968 on his progress in this area. He pointed out two major problems basic to the study of bioadhesives. First, this field of investigation is in its infancy. Not only is little information available about the chemical nature of the adhesive, but there is also very little information available about the species. Thus an investigator would have to study the species and learn basic biological processes before he could continue with the

main theme of his research. Secondly, these animals secreted micro-quantities of the adhesive and this made chemical analysis difficult.

Harrison and Philpott[47] reported at the second adhesive workshop on the work they had been doing with starfish, sea urchins, and sea cucumbers. They used the electron microscope to investigate the microstructure of glands responsible for these bioadhesives, and they also used selective stains to analyze the composition of the adhesive. Thus they were able to investigate the histochemical properties involved. Even with these sophisticated instruments, they collected very little information. Essentially they were able to locate the subcellular origin of the adhesive, and they found that acid mucopolysaccharides may be the principal chemical involved in the adhesive.

Development of New Resin Systems

The discovery that incorporating particulate material into plastics could improve the physical properties of the material led to a new area in research. With extreme heat and pressure, industrial polymer chemists had been synthesizing molecules that had low polymerization shrinkage, molecules that had a relatively low coefficient of thermal expansion, and polymers that were hard and abrasive-resistant. Then with the discovery that particles of silica, aluminas, or glass beads incorporated into a plastic matrix could produce these qualities, the prospect of making a substantial improvement over the unfilled poly (methylmethacrylate) system came into view. The polymerization shrinkage always present in the plastic systems was investigated. With the incorporation of particles

of silica or glass, the amount of polymerizable material was substantially reduced, thus decreasing the overall shrinkage. Variations in particle size and shape, as well as the type of filler material, produced changes in the physical properties of the final plastic. Dental research then became involved with this new system called "composites."

Eirich,[42] in an article describing the composite resin, stated that "the polymers are an excellent class of materials to be used as matrixes--they permit large reversible deformations with breakage, and can therefore withstand the strong and repetitive stresses at the interfaces. They also resist crack propagation better than most materials because they are able to undergo viscoelastic or plastic flow at the tips of cracks and thus dissipate large amounts of dangerous elastic energy.

Bowen[43] in 1955 made a preliminary report on a plastic restorative material composed of an epoxy resin binder impregnated with fine particles of fused silicon dioxide and porcelain. He found that this material was abrasion-resistive and possessed a crushing strength that seemed to be related to the filler. It offered the additional improvement of having less than one percent polymernization shrinkage. In a subsequent investigation in 1958, Bowen[44] found that the vinyl silane treatment of the silica filler increased the compressive strength of the composite from 11,000 psi to 16,000 psi.

As research assistant in the Materials Division of the National Bureau of Standards, Bowen did considerable work on reinforced polymers.

In 1963 he evaluated the properties of an experimental resin consisting of vinyl silane treated silica and new matrix. The silane treatment of the particle enabled more filler to be incorporated into the matrix. The resin was an addition product between bis-phenol-aand glycidyl methacrylate and was reinforced with 70% silica by weight. When compared to contemporary direct filling resins, the experimental resin had less polymerization shrinkage and thermal expansion than the poly (methylmethacrylate) direct filling resins. The compressive strength, the modulus of elasticity, and the resistance to indentation were also increased over the direct filling resins.

In the second workshop Bowen[35] alluded to the fact that resin matrixes were troubled by color instability and that recently this cause of discoloration had been attributed to planer conjugated double bonds. Two years later, Bowen and Argentar[46] reported that they had synthesized a resinous material that was color stable and had a viscosity much more suitable than the Bix-Gma system with which they had been working.

In 1964 Bowen[47] conducted some extensive research dealing with filler particle size and shape. He found that incorporating large and small particles together meant that less monomer had to be used. He also found that for a given shape and particle size mixture, the size of the particle did not change the density of the mix unless they were below a critical size. Finally Bowen showed that the strength of the composite correlated better with particle size than with precentage of resin.

Chang and Dahlman[48] in 1965 used silane-treated glass beads and fibers as a filling material. Incorporating the glass fibers in addition to the beads produced a smoother surface. The glass also aided in forming a color match to the natural tooth color because of light reflection through it. In general, these authors found an increase in strength, a decrease in thermal expansion, and a decrease in polymerization shrinkage. The properties were said to be approaching the physical properties of dentin.

Composites soon became available commercially, although several had been the subject of little or no research before they were marketed. Companies that had never marketed dental materials were now distributing samples to local dentists and making exorbitant claims about their material.[29,49] During this time,several studies were started to investigate the physical properties of these new materials.

In 1960 Bowen and Rodriguez[50] conducted tensile strength tests on a variety of dental restorative materials and samples from tooth structure. Among the materials tested was the newly developed Bis-Gma filled resin and a regular direct filling resin. The specimens were made to a specific size and stored in water at 37°c for one week and tested. No difference was observed between the two plastic materials.

Two years later a similar laboratory investigation[51] showed that treating filler particles with vincylchlorosilane increased the tensile strength of the filled resins to somewhere between those of dentin and enamel, and the modulus of elasticity of the material approached that of dentin.

In 1966 Hollenback, Allange, and Shell[52] tested the newly marketed Addent-35 with an unfilled poly (methylmethacrylate) resin. The following tests were listed as part of their study: hardness, abrasion resistance, compressive strength, transverse strength, tensile strength, adhesion, flow, dimensional change during set, and the ability of the material to receive a polish. They found that Addent had a compressive strength around 30,000 psi, a tensile strength of 5,700 psi, and a transverse strength of 6,000 psi. The new composite was much more resistant to abrasion than the unfilled acrylic.

Buonocore, Matsui, and Yakamaki[53] studied the abrasion characteristics of several restorative materials including Sevriton, silicate, Addent and amalgam. They used a tooth brushing machine and different abrasives to check the restoration for resistance to wear. The silicate and composite were comparable and much more resistant to abrasion than the amalgam or the unfilled resin.

Peterson[54] in 1966 did a comprehensive study of the physical properties of four resins, including Sevriton and Addent. Addent proved to have higher hardness and greater resistance to abrasion, but it had very poor adhesive qualities and color stability.

Custer[55] in 1969 examined the physical properties of Addent, Bonfil, Chameleon and Sevriton. The composite resins Addent and Chameleon had superior abrasion resistance and lower coefficients of thermal expansion; but they were both color unstable.

Buonocore[56] described the chemical composition of several of the new commercial resins. He said that the matrix binder in Addent and

Dakor was similar to the hybrid molecule synthesized by Bowen, namely the Bis-Gma molecule. Addent contained spherical beads of various sizes, while Dakor contained a filler of hydroxyapatite with about 20% glass beads for abrasion resistance. Both materials had comparable physical properties and were an improvement over the unfilled resins.

Macchi and Craig[57] in 1969 investigated the polishing qualities of the two composites being marketed by the 3-M Company. Addent-35 was found to contain glass beads and rods and was designated for anterior restorations. Addent 12 contained Lithium aluminum silicate and was designated as a posterior filling material. The composites gave rougher polished surfaces than the unfilled resins.

Guzman[58] in 1969 conducted a study to examine the marginal seal of Addent-35 as compared to unfilled resins. Addent-35 restorations were comparable to the unfilled resins with respect to marginal seal.

The fact that the composites have better physical properties does not mean that they will be a better restoration than unfilled resins. This is exemplified by a recent clinical study comparing the use of composite resins to amalgams in a Class II restoration.[60] Although the laboratory tests showed the amalgams to be less resistant to wear than the composite, clinically just the opposite proved to be true.

Unfortunately there is little information on clinical studies with the plastic restorations. To quote from Ryge,[59] "In view of the obvious need for clinical evaluation of any dental restorative material

it is indeed strange to note that whereas most of the accepted dental materials have been studied extensively under laboratory or in vitro conditions, practically no information is available in the literature relating such properties with the clinical acceptability of these materials."

Schulman[61] in 1965 compared paired Class III or V restorations restored with Addent, silicate, or acrylic and observed their performance at one, three and six month periods. He concluded that Addent offers promise for a more permanent type of esthetic restoration.

In 1967 Johnson, McCure, Cvar and Ryge[62] compared two epoxy and two acrylic resins to silicates in contralaterally prepared Class III and V preparations. After one year the color match was essentially the same but the silicate demonstrated more marginal breakdown and contour loss that the resins.

Bowen, Paffenbarger, and Mallimank[63] conducted a long-term clinical study comparing filled and unfilled resins to silicates. The materials were paired in Class III restorations. After four to five years, 42% of the silicates needed replacement, whereas only 4% of the resins needed replacement. There was little difference between the filled and unfilled resin.

In 1969 McCure and Associates[64] compared composite resin, amalgam, and a silicate as a posterior restorative material. They restored Class I cavities with these materials and found that after one year the marginal adaptation favored the resin and the silico-phosphate cement over the amalgam; after a three-year evaluation the silicate was still superior but the resin was not.

In a similar study[64] involving anterior teeth, hybrid epoxy resins and acrylic resins were compared with the conventional silicate cements. After both the one and three-year evaluations the resin proved to be superior to the silicate in contour and marginal integrity.

Acid Etch Technique

In retrospect it appears that one of the most promising methods of improving the adhesive strength of a resin has been the acid etch technique.[65] One of the first studies reporting the use of acid in pretreating the tooth to strengthen the restorative tooth bond was Buonocore's in 1955.[66,67] From that time on several studies have demonstrated the increased bond strength between resins and the pre-treated etched tooth. Increases in bonding strengths of over 100% have been reported in some studies.[19] Clinical reports of the use of the acid etch technique in the treatment of orthodontic cases have been encouraging.[19,68] Bond strengths strong enough to secure brackets to the enamel surface for six to seven month treatment periods were reported.

Swanson and Beck[69] in 1960 used the acid etch with Eastman 910 and a direct filling resin. They etched the enamel surface for 60 seconds with 85% phosphoric acid. Specimens run without the etching broke spontaneously after one week of water storage, whereas specimens receiving the acid etching lasted up to four weeks. When the tensile strengths were examined by applying weights to a platform suspended from the tooth by the adhesive bond, the adhesive bond created with the acid etch was decreased from 7.4 Kg to 0.9 Kg after two weeks.

In 1965 Bowen[70] used Nphenylglycine and glycidyl methacrylate as an adhesive copolymer to dentin. Dentin surfaces treated with HCL and then coated with the comonomer had a 24-hour tensile strength of 810 psi, whereas those without the treatment had bond strengths of only 630 psi. However, water decreased the adhesive bond in each case.

One year later Newman[28] demonstrated that better wetting could take place on enamel that was acid etched. Newman measured the contact angles formed by an epoxy and water on the surfaces of treated and untreated teeth. Those that were acid treated before the water was applied showed lower contact angles, indicating that the materials were wetting the surface better.

Lee and Cupples[18] in 1968 submitted a research report concerning surface pretreatment. They designated several different chemicals as to their ability to enhance adhesion to tooth structure. Phosphoric acid and sulphuric acid were among those reagents considered by the authors to be "good" pretreating agents.

In 1968 Muholland and DeShazer[71] varied the pH, molarity, and type of acids to determine the best procedure to use in the acid etch technique. From their work it can be concluded that best adhesion occurs with monovalent acids. Increases of 150 percent in bond strengths were observed. In general, adhesiveness increased as the pH of the acids was decreased from 6 to 4 to 2. Polyvalent acids, on the other hand, produced a significant increase in adhesion only when a large increase in hydrogen ion concentration occurred.

Lee[72] in 1970 did an extensive laboratory study on the adhesive properties of Sevriton when applied to an acid etched tooth surface. His most significant findings were that the acid etching greatly improved the acrylic's adhesion to enamel and that bond strength was statistically unaffected by water storage up to six months, even with thermal and stress cycling. In general, bonds with the acid etching ranged from 600-900 psi and those without ranged from 0-300 psi.

Buonocore[73] in 1970 used a mixture of three parts Bisphenol-A and glycidyl methacrylate to one part methyl methacrylate monomer to seal pit and fissures. The procedure consisted of first etching the tooth with 50% phosphoric acid and then applying the resin. Of 200 sealants originally placed, only one was lost and 195 were considered to be "excellent" in their sealing properties.

Laswell[65] in 1971 found a 60% increase in adhesion to the acid etched tooth. A high percentage of cohesive failure occurred within the resin material before the adhesive bond would break.

Doyle[74] suggested using the acid etch technique in treating fractured or traumatized incisors. These fractures commonly occur in children and an intermediate type of restoration must be used until a permanent one can be safely placed in the child's mouth.[75-83]

The possible use of this technique for fractured incisors was further investigated by Ayers,[84] who developed a procedure whereby he "halved the enamel" to get more retention with the acid etching.

After the acid etching technique became known as a promising means of increasing the adhesive bond strength, several investigators became

interested in possibly injurious effects of these procedures on the tooth. This is understandable when one realizes that this technique was being considered as a means to prophylactically reduce caries in pits and fissures by sealing those areas soon after eruption. Also, the technique was being recommended as an intermediate restoration for traumatized teeth, and as a possible means of attaching orthodontic brackets. The question as to what type of pulp reaction occurs with acid etching has not been investigated to date. However, remineralization of the acid etched surface as a potential source of damage has been studied intensively.

Albert and Grenoble[85] in 1971 used a scanning electron microscope to examine enamel surfaces treated with 50% H_3PO_4. They concluded that essentially total repair occurred after about four days.

Newman,[86] who had long been interested in orthodontic bracket attachment with the acid etch technique, also used the scanning electron microscope to examine the surface of etched teeth. He found that the roughness created after the etching procedures would return to normal.

Koulourides,[87] a noted researcher in tooth surface chemistry, examined the tooth's ability to reharden in human saliva. He used a Kentron instrument to determine the surface hardness immediately after acid etching and again after various periods of saliva storage. Normal enamel showed a KHN hardness of 325 and after etching the hardness had fallen to 180 KHN. After six hours 60 to 90% of the hardness returned and the author concluded that "human saliva has a marked ability to reharden softened enamel surfaces."

Johnson[88] in 1964 used light retardation readings in a polarizing microscope to determine that enamel was in fact remineralized by saliva. A rapid remineralization occurred during the first 24 hours, then tapered off during the next 48 hours. He found that only 50% to 60% of the total remineralization occurred and that essentially none occurred after the first three days.

Lenz and Muhlemann[89] used an electron microscope to examine the surfaces of teeth after they were treated with acid. Whereas Johnson and Koulourides had used very dilute acid solutions to get information on caries remineralization, Lenz and Muhlemann used acid solutions that were several times stronger. A pellicle formed over the etched enamel shortly after it was exposed to saliva but no remineralization occurred, as indicated by the fact that this pellicle could be removed with fine tweezers, revealing etched enamel.

EVALUATION OF ADHESION

Adhesion of the restorative materials has generally been evaluated in two ways: 1) a tensile strength test which measures the force required to pull the adhesive from the adherant, and 2) a determination of the marginal leakage of the restorative material, as this seal is considered to be some evidence of adhesion.[5] Of the two methods, the marginal seal determination probably reproduces a chemical situation more closely.

Nelson, Wolcott, and Paffenbarger[90] in 1952 coined the phrase "marginal percolation" to refer to marginal leakage they observed in several different types of restorative materials.

In 1959 Swartz[91] perfected a method of determining marginal leakage with radioactive calcium 45. Two years later Swartz and Phillips[92] published marginal leakage data on several different restorative materials using the Ca^{45} test. Two commercial acrylic preparations were among the restorative materials tested. Kadon was shown to be a less effective sealing restorative than Sevriton, which showed only a slight leakage after 24 hours imersion in radio Ca^{45}. Thermal cycling increased leakage in both cases.

Peterson[54] conducted marginal leakage studies with four acrylic resins. Addent and Sevriton were most effective in sealing the preparation and the reported reduction in the coefficient of thermal expansion for Addent was not reflected in the leakage patterns of this study.

Christen and Mitchell[93] in 1966 used fluorescent Fluorescein as an indicator in the examination of marginal leakage of dental restorations. They felt that this technique was an improvement over former marginal leakage techniques.

Tani and Buonocore[94] in 1969 varied the preparation design and the type of restorative while observing the marginal leakage. As far as the resins were concerned, Sevriton gave as good a seal as the filled resins Addent and Dakor. There was no difference in leakage patterns between shallow and deep cavities.

Going[95,96] has been involved in several studies concerning the marginal leakage of dental restorations. In a joint publication with Myers and Prussin,[97] he described a unique way of correlating <u>in vitro</u>

and in vivo studies. With this new method it was possible to test the marginal leakage of restorations under actual conditions of the oral cavity. A latex isolator was placed over the restored tooth and a manganese solution was flushed over its surface. Later, when the tooth was extracted it was placed in a nuclear reactor and the manganese was changed into a detectable radio isotope. After reviewing the results, the authors felt that the in vivo samples tested generally had more marginal leakage than their in vitro samples.

Lee and Swartz[98] in 1970 used the scanning electron microscope to observe the margins of various restorative materials. Adaptic, Addent 12, Addent 35, and Dakor were compared to a conventional filling resin, an amalgam, and a silicate cement. All specimens showed isotope leakage. However, when viewed with the scanning electron microscope, variations in marginal adaptation were observed. Lee stated that "one of the composite restorations (Adaptic) consistently showed closer cavity adaption than the amalgam tested," and that it gave a closer marginal adaptation with less marginal leakage than the other restorative materials tested.

No extensive studies have been made to determine the effect of the acid etch technique with a composite resin. All of the adhesion studies connected with the etching of tooth structure have been with the unfilled systems. Sharp and Grenoble[99] provided some indirect evidence that the acid etch technique would also work with composites. They were able to demonstrate "resin tags" on the bond interface between composites and the etched enamel. Similar tags had been described for the unfilled resins. This finding is in agreement with that of Gwinnett and Matsui.[100]

Brauer and Termini[101] recently completed a study that was started in 1970. During this time they incorporated a few samples of a composite resin (Adaptic) in their studies. They found no adhesion when this composite was placed on non-etched bovine enamel but when etched with a 5% solution of a polyvalent acid adhesive strengths of 334 psi were obtained. The main purpose of the study was to examine pretreatment agents and thus only five samples per test were run with the composite.

It seems logical that the adhesion of composites to acid etched tooth structure should be determined. That is the purpose of this thesis project.

METHODS AND MATERIALS

This study was divided into two parts. Part I evaluated the adhesive tensile bond strength by using procedures developed by Lee[72]. Part II of the study evaluated adhesion through marginal leakage by using procedures developed by Swartz[91]. In all stages of the study, manipulative procedures were standardized to conform with those of other studies.

PART I

SUBSTRATE

Extracted bovine mandibular incisors were the experimental material. The method developed by Hanke[102] was used to prepare and mount the teeth and test specimens, and to measure the adhesion of the test materials. The bovine teeth were prepared by removing the root with a diamond disc and mechanically removing the pulp tissue. The labial surfaces were flattened by grinding on a rotary wheel using wet 400 grit silicon carbide paper. Once flat, the teeth were mounted in acrylic and the surface hand ground with wet 600 grit silicon carbide paper and visually inspected for flatness with reflected light. The teeth were then stored in distilled water until ready for use. Immediately before use, each specimen was lightly reground with 600 grit silicon carbide paper to freshen the surface. Then the surface was dried with a stream of compressed air.

ACID ETCHING

A 50 percent aqueous solution of phosphoric acid was applied with a pipette for 60 seconds to the surface of the enamel. After 60 seconds, the acid was rinsed away under tap water.

ADHESION OF COMPOSITE RESINS

The composite resins used in this study were Adaptic and HL-72. They were compared to the unfilled resin Sevriton. A total of 552 samples were assigned to 46 groups of 12, which were then assembled into five principal groups. In Group I the enamel was etched and Sevriton was placed using the bead-flow technique. In Group II the enamel surfaces were etched and Adaptic was placed in accordance with the manufacturer's instructions. In Group III Adaptic resin alone was placed on unetched enamel. In Group IV the enamel surfaces were etched and HL-72 was placed in accordance with the manufacturer's instructions. In Group V HL-72 resin alone was placed on unetched enamel.

A split silicone ring matrix was used to confine the resin material. A brass ring was slipped over the outside of the silicone matrix to maintain the dimensions; the matrix was carefully positioned over the enamel surface and held in place with nail polish applied to the under surface of the silicone matrix. For specimens in Group I, Sevriton cavity sealer was applied to the enamel with a fine camel hair brush. The Sevriton was applied from dappen dishes with a brush using the bead-flow technique.[29] When Adaptic or HL-72 was used, a bulk-pack method of placing the material was used. In order to prevent air voids, the resin mass was teased over the enamel with a rubber gingival stimulator. When the matrix was filled, a hole drilled in a brass ball was filled with resin and placed over the silicone matrix with gentle finger pressure.[102] Then the resin was allowed to set under the weight

of the ball alone.[102] This ball served as an attachment for securing the specimen in the grips of the testing machine for subsequent tests to determine bond strength. After initial polymerization, the specimens were stored in a glass container at 37°C at 100% humidity for 30 minutes to allow more complete polymerization before the matrix was removed and the specimens were stored in water.

METHODS OF TESTING

The following tests were conducted to determine their effects on the adhesive bonds: storage time in water, temperature stressing, and intermittent tensile stressing, and the combination of temperature stressing and tensile stressing.

Storage in Water

Twelve specimens for each of Groups 2 through 5 were stored in distilled water at 37°C for 24 hours, 30 days, and 6 months. Twelve specimens for Group I were stored for 24 hours only. At completion of the respective storage times, the test specimens were subjected to a tensile test to measure the bond strength. Each specimen was held in a special jig mounted on a Rhiele testing machine. A tensile load was applied at a cross head speed of 0.030 inches per minute until bond failure.

Temperature Stressing

Twelve specimens for each of Groups 2 through 5 were first stored for 24 hours, 30 days, and 6 months at 37°C and then temperature cycled before testing. Twelve specimens for Group I were stored for 24 hours only and then temperature cycled before testing. Using an automatic

temperature cycling apparatus, the test specimens were alternately cycled 500 times between two water baths. The temperature range of these baths was between 10°C and 50°C, which is the approximate temperature change that occurs orally when hot and cold foods are ingested.[54] The bond strength of the specimens was then tested by applying a tensile load at the rate of 0.030 inches per minute.

Mechanical Stressing

Twelve specimens for each of Groups 2 through 5 were first stored for 24 hours, 30 days and 6 months at 37°C and then subjected to intermittent tensile stressing. Twelve specimens for Group I were stored for 24 hours only and then subjected to intermittent tensile stressing. Each specimen was subjected to a load of 300 psi at a cross head speed of 0.50 inches per minute. Upon reaching 300 lbs. the load was released and reapplied at the same rate. At completion of 60 cycles the specimen was subjected to a tensile load at a rate of 0.030 inches per minute until bond failure occurred.

Temperature and Mechanical Stressing

Twelve specimens for Group II and IV only were first stored in water at 37°C for 24 hours, 30 days, and 6 months and then subjected to stress cycling and temperature cycling as previously described. Twelve specimens of Group I were stored for 24 hours only and then subjected to stress cycling and temperature cycling. Next the specimens were subjected to a tensile load at a rate of 0.030 inches per minute until bond failure.

Each specimen was kept moist during all manipulative procedures[102] and each specimen was examined to determine if failure occurred adhesively or cohesively.

PART II

MARGINAL LEAKAGE

Extracted human teeth were restored with the same three resins used in Part I of this study, and the effect of temperature cycling on the marginal seal was observed in relation to the acid etching of the cavity preparation.

Class V cavity preparations were cut in the middle third of the labial surface of the crowns of 120 extracted human canine and bicuspid teeth. The cavity was prepared with a 557 carbide bur in an air rotor and finished with a 557 steel bur and low speed.

Sixty preparations were etched with a cotton pledget of 50% phosphoric acid for 60 seconds and then rinsed with tap water and blown dry with compressed air. The other 60 prepared teeth not etched with acid were rinsed with tap water and dried with air.

The composite resins were placed in the restorations with the bulk-pack technique. A cellophane matrix strip was used to hold pressure on the resin and keep air from its surface until final set.[29] The Sevriton resin was placed with the bead-flow method. Fifteen minutes later all restorations were finished.

The 120 specimens were divided into two groups, with 30 etched and 30 non-etched specimens in each group. Group I specimens were

placed in distilled water at 37°C for one week. Group II specimens were thermally cycled 2500 times, using the same immersion time and temperature settings as in Part I of this study.

The marginal seal was assessed by infiltration of radioactive calcium 45. Leakage was revealed by autoradiographs. The procedure was one developed by Swartz[91] and used in several similar studies.[54,72]

The teeth were covered with clear finger nail polish so that only the periphery of the restoration and tooth structure was exposed. Tin foil was then wrapped around the teeth, exposing only the restoration. The edges of the tin foil were sealed with finger nail polish. The teeth were immersed in 0.1 MC/ML solution of calcium 45 for two hours. Upon removal, the teeth were rinsed with tap water, and then scrubbed with detergent before and after removal of the tin foil. The teeth were sectioned longitudinally through the restoration by means of a gillings Hamco sectioning machine. The tooth sections were placed, cut surfaces down, on an ultra high speed dental x-ray film supported by a plastic slab. The tooth was held in position with a rubber band.

This assembly was wrapped in tin foil and placed in a light proof container for 17 hours. The film was processed and developed with routine dark room procedures. The resultant autoradiographs were visually examined for penetration of the isotope at the margins of the restorations.

RESULTS

PART I

Adhesion of Composite and Direct Filling Resins

Storage in Water

The results of the tests conducted on specimens stored in water at a constant temperature of 37°C for 24 hours, 30 days, and 6 months are shown in Tables I, II and III and the data are summarized in Figures 7,8, and 9.

Regardless of the storage time or the resin employed, in most instances the control specimens of Group III (Adaptic with no acid etch) and Group V (HL-72 with no acid etch) separated during the storage period or during their insertion into the tensile testing machine. 26 of the 36 control Adaptic specimens and 31 of the 36 control HL-72 specimens failed before or during insertion into the testing machine. The specimens all failed in adhesion.

Very few specimens in Group I (Sevriton with acid etch), Group II (Adaptic with acid etch), and Group IV (HL-72 with acid etch) failed to survive the storage times. Only two of 36 specimens in Group IV (HL-72 with acid etch) and none of the corresponding Sevriton or Adaptic specimens failed prior to tensile testing. The average bond strength values for the Group I series (Sevriton with acid etch) of specimens were 869±17 psi at 24 hours, 1136±199 psi at 30-days* and 1030±179 psi at 6 months.* An adhesive-cohesive type separation occurred in all specimens. The average bond strength values for the Group II series (Adaptic with acid etch) of specimens were 947±62 psi at 24 hours, 812±162 psi at 30 days,

*Values obtained from Lee's[72] study

and 453±143 psi at 6 months. In most cases an adhesive separation occurred, that is, the specimen failed at the resin-tooth interface.

The average bond strength values for the Group IV series (HL-72 with acid etch) of specimens were 947±62 psi at 24 hours, 734±304 psi at 30 days, and 741±321 psi at 6 months. The specimens also failed in adhesion.

Thermal Stress

The results of the tests conducted at 24 hours, 30 days, and 6 months on specimens which had been subjected to thermal cycling appear in Tables I, IV, and V and are summarized in Figures 7,8, and 9.

Regardless of storage times, all control specimens of Group III (Adaptic with no acid etch) and Group V (HL-72 with no acid etch) separated during the thermal cycling procedure or during insertion into the tensile testing machine. The failures were adhesive.

Independent of storage times, the majority of the specimens in Group I (Sevriton with acid etch), Group II (Adeptic with acid etch), and Group IV (HL-72 with acid etch) survived the thermal stress cycling. Only two of the 36 Adaptic specimens in Group II, eight of the 36 specimens in Group IV (HL-72 with acid etch), and none of the specimens in Group I (Sevriton with acid etch) failed prior to tensile testing. The average bond strength values for the Group I series (Sevriton with acid etch) specimens were 834±273 psi at 24 hours, 956±272 psi at 30 days,* and 842±192 psi at 6 months.* The type of failure which predominated was adhesive-cohesive. The average bond strength values for the Group II

*Values obtained from Lee's[72] study.

series (Adaptic with acid etch) of specimens were 647±264 psi at 24 hours, 759±123 psi at 30 days, and 506±128 psi for 6 months. The primary type of failure was adhesive. The average bond strengths for Group IV (HL-72 with acid etch) specimens were 312±245 psi at 24 hours, 341±260 psi at 30 days, and 493±285 psi at 6 months. The bonds failed in adhesion.

Regardless of the type of material used, thermal cycling reduced the retention more than did storage in water at a constant temperature. Increasing the storage times in water prior to stressing did not appear to appreciably lower bond strengths of the resins in Groups I and IV and lowered bond strengths only slightly in Group II (Adaptic with acid etch).

Mechanical Stress

The results of the test conducted at 24 hours, 30 days, and 6 months on specimens which were mechanically stressed appear in Tables I, VI and VII and are summarized in Figures 7,8, and 9.

Regardless of the storage time or the resin used, all control specimens of Group III (Adaptic with no acid etch) and Group V (HL-72 with no acid etch), separated during the mechanical stress cycling procedure or during insertion into the tensile testing machine. All specimens in Group I (Sevriton with acid etch), 26 of the 36 specimens in Group II (Adaptic with acid etch), and 25 of the 36 experimental specimens in Group IV (HL-72 with acid etch) survived mechanical stress cycling. The average bond strength values for the Group I (Sevriton with acid etch) series of test specimens were 923±52 psi at 24 hours, 862±275 psi at 30

days,* and 1029±130 psi at 6 months,* an adhesive-cohesive type separation occurred in all specimens. The average bond strength values for Group II (Adaptic with acid etch) series of test specimens were 682±508 psi at 24 hours, 1073±279 psi at 30 days, and 342±325 psi at 6 months. The bond failure was predominantly adhesive. The average bond strengths for Group IV (HL-72 with acid etch) specimens were 503±345 psi at 24 hours, 411±243 psi at 30 days, and 793±321 psi at 6 months. The bond failed in adhesion.

Regardless of the type of resin used, a decrease in retention was observed in acid etched groups when the specimens were subjected to stress cycling. The decrease in retention appeared to be less, however, than what was observed when the same resin was thermal cycled.

Temperature and Mechanical Stress

Results of the tests conducted on specimens which were both thermal and stress cycled following 24 hours, 30 days, and 6 months storage in water appear in Tables I, VIII, and IX and are summarized in Figures 7,8, and 9.

The average bond strength values for the Group I (Sevriton with acid etch) series of test specimens were 924±133 psi at 24 hours, 908±236 psi at 30 days,* and 787±284 at 6 months.* A major portion of the specimens failed in an adhesive-cohesive manner. The average bond strength values for the Group II (Adaptic with acid etch) series of test specimens were 989±355 psi at 24 hours, 845±295 psi at 30 days, and 152±251 psi at 6 months with bond separation occurring in adhesion.

*Values obtained from Lee's[72] study.

The average bond strength values for the Group IV (HL-72 with acid etch) series of test specimens were 656±465 psi at 24 hours, 220±296 psi at 30 days, and 236±355 psi at 6 months. The bonds separated in adhesion.

Regardless of the resin used, the tensile bond values of the thermal and mechanical stressed specimens decreased with increased storage time. These values were the lowest obtained in any of the experiments.

Statistical Analysis

A complex statistical analysis comparing each of the forty-six groups and test conditions was not considered useful for practical application. However, all the acid etched specimens from one resin at each storage time, considered as a group, were analyzed by an analysis of variance, and a Newman-Keul method of individual comparison was used to determine significant trends.

The different resin materials were compared at 24 hours, 30 days, and 6 months storage. At 24 hours, an analysis of variance showed that there was a significant difference between the three resins. ($F=8.37$ with 0.0005 level of confidence) The two tailed t Newman-Keul analysis showed that this difference was between Sevriton and HL-72, in which the Sevriton specimen were significantly more retentive at 24 hours. ($t=4.02$ when 3.01 value was required for 0.01 level of confidence). At 30 days Adaptic was significantly more retentive than HL-72. ($t=4.18$ when 2.63 value was required for a 0.01 level of confidence). At 6 months, however, HL-72 was significantly more retentive than Adaptic.

(t=2.28 when 1.99 value was required for a 0.05 level of confidence).

The adhesion of the composite resins was then analyzed for the effects of storage time. An analysis of variance of Adaptic specimens at 24 hours, 30 days, and 6 months indicated that there was a significant difference. (F=11.63 when 4.75 values were required for a 0.01 level of confidence.) The Newman-Keul analysis showed a significant retention loss between 24-hour and 6-month specimens; (t=3.61 with a 0.001 level of probability) and a significant retention loss between 30-day and 6 month specimens. (t=5.37 with a 0.000 level of probability). An analysis of variance of HL-72 specimens at 24 hours, 30 days, and 6 months indicated no significant difference. (F-1.11 when 3.06 value was needed at a 0.05 level of confidence. The Newman-Keul analysis also showed no significant difference between HL-72 specimens stored for 24 hours, 30 days and 6 months.

PART II

Marginal Leakage

The results of isotope tests conducted to compare the adaptation of two composite resins to an unfilled resin placed with and without etching of the enamel are presented in Figures 10-14. Three autoradiographs were selected as representative of the results obtained from each group and each test condition.

One Week Storage in Water

The control composite restorations of Adaptic and HL-72 stored in distilled water at 37^{o}C for one week exhibited approximately the same

amount of isotope penetration. As can be seen in Figures 11-12, marginal leakage was slight.

After one week storage, both the unfilled resin (Sevriton) and the composite resins (Adaptic and HL-72) when placed in etched preparations showed virtually no marginal penetration of the radioisotope. These autoradiographs can be seen in Figures 10, 11 and 12.

Thermal Stress

The control composite restorations for Adaptic and HL-72 which were stored in distilled water at 37°C for one week and subjected to 2500 temperature cycles at a 40°C temperature differential exhibited comparable marginal leakage, which was slightly more than for specimens not subjected to thermal cycling. Typical leakage patterns appear in Figures 13 and 14.

After one week storage in water followed by thermal cycling, both the unfilled resin (Sevriton) and the composite resins (Adaptic and HL-72) when placed in etched preparations exhibited about the same marginal leakage (Figures 10,13, and 14). The composite resins placed in acid etched restorations showed slightly less leakage than the unetched counter parts (Figures 13 and 14).

TABLES

ADHESION OF SEVRITON TO ENAMEL
24 HOURS STORAGE IN WATER AT 37 C

	STORAGE ONLY		THERMAL** CYCLE		STRESS*** CYCLE		THERMAL**& STRESS*** CYCLE	
	GROUP I (acid)		GROUP I (acid)		GROUP I (acid)		GROUP I (acid)	
Spec. no.	psi	Type of break	psi	Type of break	psi	Type of break	psi	Type of break
1	1019.2	A-C	828.1	A-C	1219.4	A-C	1501.5	C
2	592.4	A-C	869.1	A-C	819.0	A-C	705.3	A-C
3	964.6	A-C	445.9	A-C	1092.0	A-C	987.4	A-C
4	928.2	A-C	891.8	A-C	682.5	A-C	850.9	A-C
5	782.6	A-C	1283.1	A-C	823.6	A-C	773.5	A-C
6	1128.4	A-C	759.9	A-C	755.3	A-C	623.4	A-C
7	1011.0	A-C	1192.1	A-C	1028.3	A-C	1014.7	A-C
8	700.7	A-C	450.5	A-C	809.9	A-C	609.7	A-C
9	664.3	A-C	1305.9	A-C	873.6	A-C	873.6	A-C
10	646.1	A-C	573.3	A-C	1014.7	A-C	773.5	A-C
11	828.1	A-C	445.9	A-C	Disqualified		1155.7	A-C
12	1164.8	A-C	964.6	A-C	1032.9	A-C	1214.9	A-C
Average	869.2		834.2		922.8		923.7	
S.D.	17.79		272.6		51.69		133.3	

A= Adhesive
C= Cohesive
A-C= Adhesive & Cohesive

**Temperature Differential - 40 C
500 Cycles - 30 sec
***300 psi/cycle, 60 cycles at a rate of 0.50 inches/minute, then broken at a rate of 0.030 inches/minute

TABLE I

ADHESION OF ADAPTIC TO ENAMEL
STORAGE IN WATER AT 37°C **

Spec. no.	24HOURS GROUP II (acid) psi	Type of break	24HOURS GROUP III (control) psi	Type of break	30 DAYS GROUP II (acid) psi	Type of break	30 DAYS GROUP III (control) psi	Type of break	6 MONTHS GROUP II (acid) psi	Type of break	6 MONTHS GROUP III (control) psi	Type of break
1	1557.0	A-C	0	A	1301.3	A	22.75	A	313.95	A	59.15	A
2	1060.2	A-C	0	A	254.8	A	354.9	A	664.30	A	0	A
3	955.5	A	0	A	1078.4	A	113.8	A	687.1	A	0	A
4	691.0	A	0	A	500.5	A	31.85	A	1137.5	A	0	A
5	573.3	A	0	A	132.0	A	182.0	A	150.15	A	0	A
6	910.0	A	0	A	1123.9	C	77.35	A	313.95	A	18.20	A
7	755.3	A	0	A	1092.0	A	0	A	68.25	A	0	A
8	1247.6	A	0	A	1042.0	A	0	A	177.45	A	0	A
9	Disqualified				878.2	A	0	A	577.85	A	0	A
10	Disqualified				614.3	A	177.5	A	473.2	A	0	A
11	1428.7	A	0	A	1246.7	A	168.4	A	391.3	C	0	A
12	291.2	A	0	A	482.3	A	0	A	482.3	A	0	A
Average	947.0		0		812.2		94.05		453.1		6.45	
S.D.	61.74		0		161.5		84.98		143.4		16.28	

A= Adhesive
C= Cohesive
A-C = Adhesive & Cohesive

**Cross head speed - 0.030 inches/minute

TABLE II

ADHESION OF HL-72 TO ENAMEL
STORAGE IN WATER AT 37 C**

Spec. no.	24 HOURS GROUP IV (acid) psi	Type of break	24 HOURS GROUP V (control) psi	Type of break	30 DAYS GROUP IV (acid) psi	Type of break	30 DAYS GROUP V (control) psi	Type of break	6 MONTHS GROUP IV (acid) psi	Type of break	6 MONTHS GROUP V (control) psi	Type of break
1	646.1	A	0	A	1683.5	A	0	A	418.6	A	0	A
2	1469.7	A	0	A	623.4	A	9.1	A	1283.1	C	0	A
3	391.3	A	0	A	1779.1	A	0	A	1169.4	A	0	A
4	991.9	A	182.0	A	68.3	A	0	A	1465.1	A	0	A
5	414.1	A	0	A	800.8	C	0	A	550.6	A	0	A
6	236.6	A	0	A	86.5	A	0	A	91.00	A	0	A
7	1369.6	C	72.8	A	496.0	A	0	A	1005.6	C	0	A
8	427.7	A	45.5	A	1014.7	A	0	A	423.2	A	0	A
9	141.1	A	31.9	A	304.9	A	0	A	0	A	0	A
10	955.5	A	0	A	1478.8	A	0	A	905.5	A	0	A
11	236.6	A	0	A	200.2	A	0	A	0	A	0	A
12	1069.3	A	0	A	286.2	A	0	A	1574.3	A	0	A
Average	947.0		27.7		733.7		-		740.5			
S.D.	61.7		48.8		304.2		-		321.1			

A = Adhesion
C = Cohesion
A-C = Adhesion & Cohesion

**Cross head speed - 0.030 inches/minute

TABLE III

ADHESION OF ADAPTIC TO ENAMEL
STORAGE IN WATER AT 37°C, THERMAL CYCLE**

Spec. no.	24 HOURS GROUP II (acid) psi	Type of break	24 HOURS GROUP III (control) psi	Type of break	30 DAYS GROUP II (acid) psi	Type of break	30 DAYS GROUP III (control) psi	Type of break	6 MONTHS GROUP II (acid) psi	Type of break	6 MONTHS GROUP III (control) psi	Type of break
1	1073.8	A-C	0	A	1028.3	A	0	A	832.65	A	0	A
2	68.25	A	0	A	514.2	A	0	A	664.30	A	0	A
3	9.10	A	0	A	72.80	A	0	A	532.35	A	0	A
4	1155.7	C	0	A	1160.3	A-C	0	A	464.10	A	0	A
5	27.3	A	0	A	919.1	A-C	0	A	309.4	A	0	A
6	218.4	A	0	A	527.8	A	0	A	414.1	A	0	A
7	1137.5	A	0	A	368.6	A	0	A	910.0	A	0	A
8	828.1	A	0	A	1333.2	A	0	A	559.7	A	0	A
9	1374.1	C	0	A	691.6	A	0	A	682.5	A	0	A
10	218.4	A	0	A	1224.0	A-C	0	A	509.6	A	0	A
11	0	A	0	A	1046.5	A	0	A	0	A	0	A
12	1656.2	A	0	A	159.3	A	0	A	186.6	A	0	A
Average	647.2		0		753.8				505.45		0	
S.D.	263.8		0		123.4				128.2		0	

A = Adhesive
C = Cohesive
A-C = Adhesive & Cohesive

**Temperature differential - 40°C
500 cycles - 30 seconds, then broken at a rate of 0.030 inches/minute

TABLE IV

ADHESION OF HL-72 TO ENAMEL
STORAGE IN WATER AT 37 C, THERMAL CYCLED**

	24 HOURS				30 DAYS				6 MONTHS			
	GROUP IV (acid)		GROUP V (control)		GROUP IV (acid)		GROUP V (control)		GROUP IV (acid)		GROUP V (control)	
Spec. no.	psi	Type of break	psi	Type of break	psi	Type of break	psi	Type of break	psi	Type of break	psi	Type of break
1	154.7	A	0	A	1173.9	A	0	A	0	A	0	A
2	45.5	A	0	A	54.6	A	0	A	1069.3	A	0	A
3	81.9	A	0	A	641.6	A	0	A	0	A	0	A
4	336.7	A	0	A	0	A	0	A	668.9	A	0	A
5	705.3	A	0	A	550.6	A	0	A	104.7	A	0	A
6	1123.9	C	0	A	432.3	A	0	A	737.1	A	0	A
7	0	A	0	A	332.2	A	0	A	932.8	A	0	A
8	236.6	A	0	A	223.0	A	0	A	1082.9	A	0	A
9	163.8	A	0	A	564.2	A	0	A	555.1	A	0	A
10	609.7	A	0	A	113.8	A	0	A	0	A	0	A
11	209.3	A	0	A	0	A	0	A	0	A	0	A
12	77.4	A	0	A	0	A	0	A	764.4	A	0	A
Average	312.1		0		340.5		0		492.9			
S.D.	245.1		0		259.5		0		284.7			

A = Adhesion
C = Cohesion
A-C = Adhesion & Cohesion

**Temperature differential - 40 C
500 cycles - 30 seconds
cross head speed - 0.030 inches/minute

TABLE V

ADHESION OF ADAPTIC TO ENAMEL
STORAGE IN WATER AT 37 C, STRESS CYCLE**

Spec. no.	24 HOURS GROUP II (acid) psi	Type of break	24 HOURS GROUP III (control) psi	Type of break	30 DAYS GROUP II (acid) psi	Type of break	30 DAYS GROUP III (control) psi	Type of break	6 MONTHS GROUP II (acid) psi	Type of break	6 MONTHS GROUP III (control) psi	Type of break
1	0	A	0	A	982.8	A	0	A	382.8	A	0	A
2	887.3	A	0	A	882.7	A	0	A	1164.8	A	0	A
3	518.7	A	0	A	Disqualified		0	A	0	A	0	A
4	0	A	0	A	0	A	0	A	395.9	A	0	A
5	Disqualified		0	A	814.5	A	0	A	0	A	0	A
6	1360.5	A	0	A	373.1	A	0	A	0	A	0	A
7	491.4	A	0	A	1042.0	A-C	0	A	618.8	A	0	A
8	946.4	C	0	A	1169.4	A	0	A	900.9	A	0	A
9	Disqualified		0	A	1606.2	A-C	0	A	0	A	0	A
10	1929.2	A-C	0	A	1383.2	A-C	0	A	641.6	A	0	A
11	Disqualified		0	A	1697.2	C	0	A	0	A	0	A
12	0	A	0	A	1847.3	A-C	0	A	0	A	0	A
Average	681.5		0		1072.6		0		342.0		0	
S.D.	508.4		0		279.3		0		324.8		0	

A = Adhesive
C = Cohesive
A-C = Adhesive & Cohesive

**300 psi/cycle, 60 cycles at a rate of 0.50 inches/minute, then broken at a rate of 0.030 inches/minute

TABLE VI

ADHESION OF HL - 72 TO ENAMEL
STORAGE IN WATER AT 37 C, STRESS CYCLED**

Spec. no.	24 HOURS				30 DAYS				6 MONTHS			
	GROUP IV (acid)		GROUP V (control)		GROUP IV (acid)		GROUP V (control)		GROUP IV (acid)		GROUP V (control)	
	psi	Type of break	psi	Type of break	psi	Type of break	psi	Type of break	psi	Type of break	psi	Type of break
1	0	A	0	A	846.3	A	0	A	0	A	0	A
2	814.5	A	0	A	514.2	A	0	A	673.4	A	0	A
3	0	A	0	A	869.1	A	0	A	1078.4	A	0	A
4	0	A	0	A	455.0	A	0	A	414.1	C	0	A
5	0	A	0	A	0	A	0	A	1123.9	A	0	A
6	1242.2	A	0	A	477.8	A	0	A	955.5	A	0	A
7	1032.9	C	0	A	0	A	0	A	1446.9	A	0	A
8	477.8	A	0	A	0	A	0	A	641.6	A	0	A
9	1028.3	A	0	A	505.1	A	0	A	1610.7	C	0	A
10	809.9	A	0	A	377.7	A	0	A	809.9	A-C	0	A
11	627.9	A	0	A	887.3	A	0	A	759.9	A	0	A
12	0	A	0	A	0	A	0	A	0	A	0	A
Average	502.8		0		411.0		0		792.9			
S.D.	345.1		0		243.3		0		320.9			

A = Adhesion
C = Cohesion
A-C = Adhesion & Cohesion

**300 psi/cycle, 60 cycles at a rate of 0.50 inches/minute, then broken at a cross head speed of 0.030 inches/minute

TABLE VII

ADHESION OF ADAPTIC TO ENAMEL
STORAGE IN WATER AT 37 C, TEMPERATURE** & STRESS CYCLING***

Spec. no.	24 HOURS GROUP II (acid) psi	Type of break	30 DAYS GROUP II (acid) psi	Type of break	6 MONTHS GROUP II (acid) psi	Type of break
1	618.8	A	678.0	A	733.5	A
2	764.4	A	555.1	A	0	A
3	1638.0	A-C	787.2	C	0	A
4	1137.5	A	0	A	418.6	A
5	1110.2	A	Disqualified		0	A
6	1647.1	A-C	468.7	A	0	A
7	0	A	837.2	A	0	A
8	354.9	A	1401.4	C	0	A
9	2065.7	A-C	864.5	A-C	0	A
10	541.5	A	1651.7	A-C	637.0	A
11	1005.6	A	1255.8	A	0	A
12	Disqualified		796.3	A	0	A
Average	989.4		845.1		152.4	
S. D.	354.6		294.9		250.7	

A = Adhesive
C = Cohesive
A-C = Adhesive & Cohesive

**Temperature differential - 40 C
500 cycles - 30 seconds
***300 psi/cycle, 60 cycles at a rate of 0.50 inches/minute then broken at a rate of 0.030 inches/minute

TABLE VIII

ADHESION OF HL-72 TO ENAMEL
STORAGE IN WATER AT 37 C, TEMPERATURE** & STRESS CYCLING***

Spec. no.	24 HOURS GROUP IV (acid) psi	Type of break	30 DAYS GROUP IV (acid) psi	Type of break	6 MONTHS GROUP IV (acid) psi	Type of break
1	1760.9	A	0	A	0	A
2	0	A	0	A	0	A
3	0	A	1028.3	A	568.8	A
4	536.9	A	477.8	A	0	A
5	705.3	A	559.7	A	0	A
6	978.3	A	0	A	0	A
7	1178.5	A	0	A	450.5	A
8	1578.3	A	0	A	509.6	C
9	0	A	0	A	0	A
10	414.1	A	577.9	A	1310.4	A
11	728.0	A	0	A	0	A
12	0	A	0	A	0	A
Average	656.4		220.3		236.6	
S.D.	464.5		295.8		354.7	

A = Adhesive
C = Cohesive
A-C = Adhesive & Cohesive

**Temperature differential - 40 C
500 cycles - 30 seconds
***300 psi/cycle, 60 cycles at a rate of 0.50 inches/minute, then broken at a rate of 0.030 inches/minute

TABLE IX

ANALYSIS OF VARIANCE IN STORAGE TIME
OF ADAPTIC AND HL-72 ACID ETCHED SPECIMENS
STORED 24 HOURS, 30 DAYS, AND 6 MONTHS

MATERIAL	SAMPLE SIZE	MEAN	VARIANCE	STD. DEV.	F-VALUE	CRITICAL VALUE 0.05	CRITICAL VALUE 0.01
ADAPTIC @ 24 HRS.	48	713.62	371446.83	609.46			
ADAPTIC @ 30 DAYS	48	832.97	23562.69	485.41	11.63	3.06	4.75
ADAPTIC @ 6 MONTHS	48	362.43	112536.85	335.47			
HL-72 @ 24 HRS.	48	541.84	244382.19	494.35			
HL-72 @ 30 DAYS	48	426.77	213616.89	462.19	1.11	3.06	4.75
HL-72 @ 6 MONTHS	48	565.73	269227.76	518.87			

TABLE X

NEWMAN-KEUL METHOD OF INDIVIDUAL COMPARISONS
OF ADAPTIC AND HL-72 ACID ETCHED SPECIMENS STORED 24 HRS., 30 DAYS, AND 6 MONTHS

MATERIAL	SAMPLE SIZE	MEAN	VARIANCE	STD. DEV.	t-VALUE	PROB.
ADAPTIC @ 24 HRS.	48	713.62	371446.83	609.46		
					-1.01	0.320
ADAPTIC @ 30 DAYS	48	830.97	235626.69	485.41		
ADAPTIC @ 24 HRS.	48	713.62	371446.83	609.46		
					3.61	0.001
ADAPTIC @ 6 MONTHS	48	362.42	112536.85	335.47		
ADAPTIC @ 30 DAYS	48	830.97	235626.69	485.41		
					5.37	0.000
ADAPTIC @ 6 MONTHS	48	362.42	112536.85	335.47		
HL-72 @ 24 HRS.	48	541.84	244382.19	494.35		
					1.15	0.254
HL-72 @ 30 DAYS	48	426.77	213616.89	462.19		
HL-72 @ 24 HRS.	48	541.84	244382.19	494.35		
					-0.27	0.785
HL-72 @ 6 MONTHS	48	565.73	269227.76	518.87		
HL-72 @ 30 DAYS	48	426.77	213616.89	462.19		
					-1.50	0.141
HL-72 @ 6 MONTHS	48	565.73	269227.76	518.87		

TABLE XI

ANALYSIS OF VARIANCE BETWEEN RESIN MATERIALS
WHEN ACID ETCHED AND STORED 24 HRS, 30 DAYS AND 6 MONTHS

MATERIAL	SAMPLE SIZE	MEAN	VARIANCE	STD. DEV.	F-VALUE	PROB.
ADAPTIC @ 24 HRS.	48	713.62	371446.83	609.46		
					8.37	0.0005
HL-72 @ 24 HRS.	48	541.84	244382.19	494.35		
SEVRITON @ 24 HRS.	48	868.25	72197.73	268.70		
ADAPTIC @ 30 DAYS	48	830.97	23562.69	485.41		
					17.46	0.00007
HL-72 @ 30 DAYS	48	426.77	213616.89	462.19		
ADAPTIC @ 6 MONTHS	48	362.43	112536.85	335.47		
					5.20	0.003
HL-72 @ 6 MONTHS	48	565.73	269227.76	518.87		

TABLE XII

NEWMAN-KEUL METHOD OF INDIVIDUAL COMPARISONS BETWEEN RESIN MATERIALS WHEN ACID ETCHED AND STORED 24 HRS., 30 DAYS AND 6 MONTHS

MATERIAL	SAMPLE SIZE	MEAN	VARIANCE	STD. DEV.	t-VALUE	CRITICAL VALUES 0.05	0.01
SEVRITON @ 24 HRS.	48	863.25	72197.74	268.70			
					4.02	2.40	3.01
HL-72 @ 24 HRS.	48	541.84	244382.19	494.35			
SEVRITON @ 24 HRS.	48	868.25	72197.74	268.70			
					1.61	2.00	2.66
ADAPTIC @ 24 HRS.	48	713.62	371446.83	609.46			
ADAPTIC @ 24 HRS.	48	713.62	371446.83	609.46			
					1.52	1.99	2.64
HL-72 @ 24 HRS.	48	541.84	244382.19	494.35			
ADAPTIC @ 30 DAYS	48	830.70	235626.69	485.41			
					4.18	1.99	2.63
HL-72 @ 30 DAYS	48	426.77	213616.89	462.19			
ADAPTIC @ 6 MONTHS	48	362.43	112536.85	335.47			
					2.28	1.99	2.64
HL-72 @ 6 MONTHS	48	565.73	269227.76	518.87			

TABLE XIII

ILLUSTRATIONS

Figure 1. Bovine tooth prepared for mounting and specimen mounted in acrylic resin

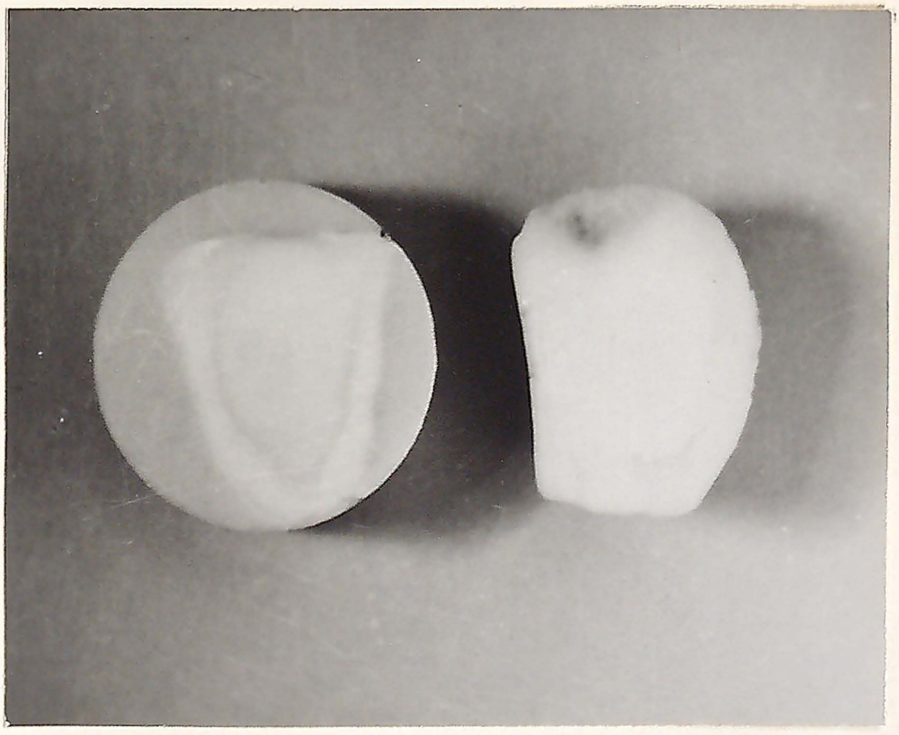


Figure 2. Photograph of mounted test specimen.

Figure 3. Cross section of adhesion test specimen

A. Brass ball bearing.
B. Adhesive.
C. Excess adhesive.
D. Silicon matrix.
E. Brass ring for stabilizing matrix.
F. Bovine tooth.

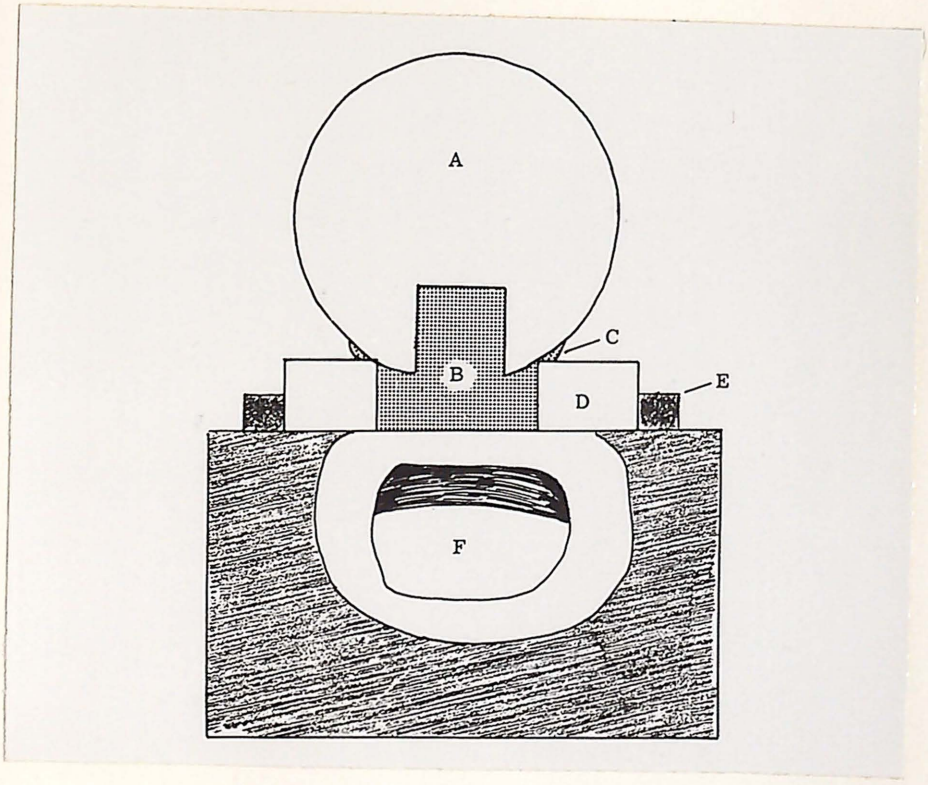

A
B
C
D
E
F

Figure 4. Diagram of adhesion testing apparatus for mounting into testing machine. A. Brass ring; B. Brass support plate pivoted off of brass ring; C. Support plate pivoted off support plate B; D. Test specimen; E. Slotted brass tube to serve as attachemnt of specimen in tensile grips; F. Wires for attachment in grips of tensile test machine. All joints are freely movable to permit proper alignment of specimen during testing.

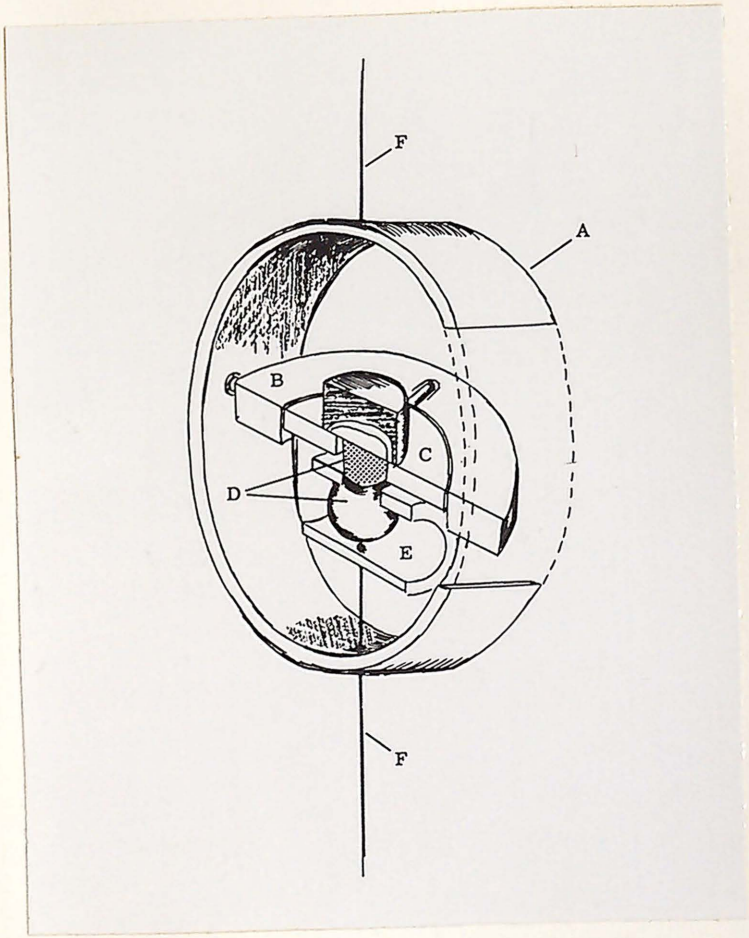

F
A
B
C
D
E
F

Figure 5. Temperature cycling apparatus. The specimens were placed in the wire mesh container and cycled between the two water baths. The temperature differential was controlled by the water circulating through the metal tanks. The automatic timer and counting device can be seen on the control panel to the right.

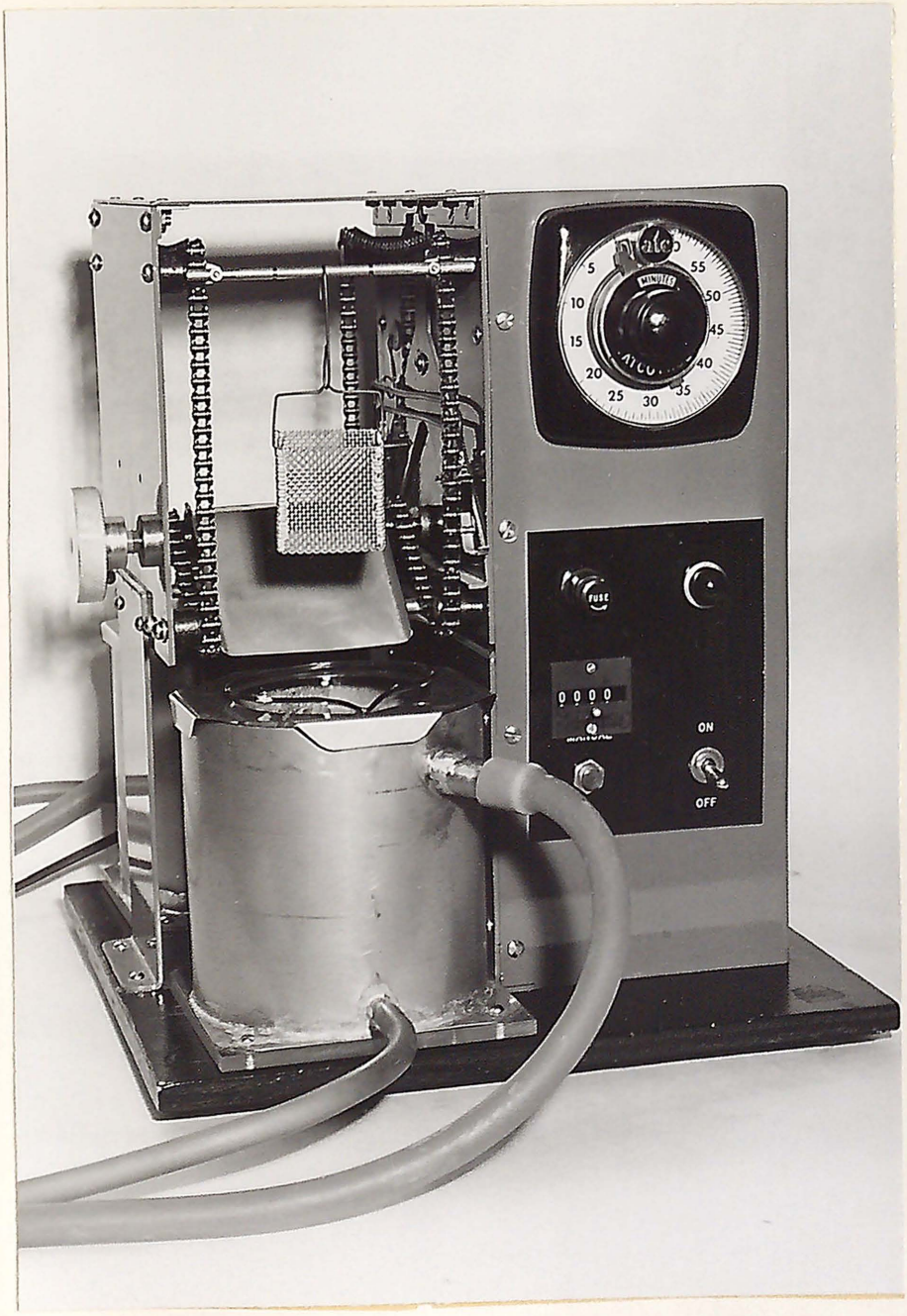
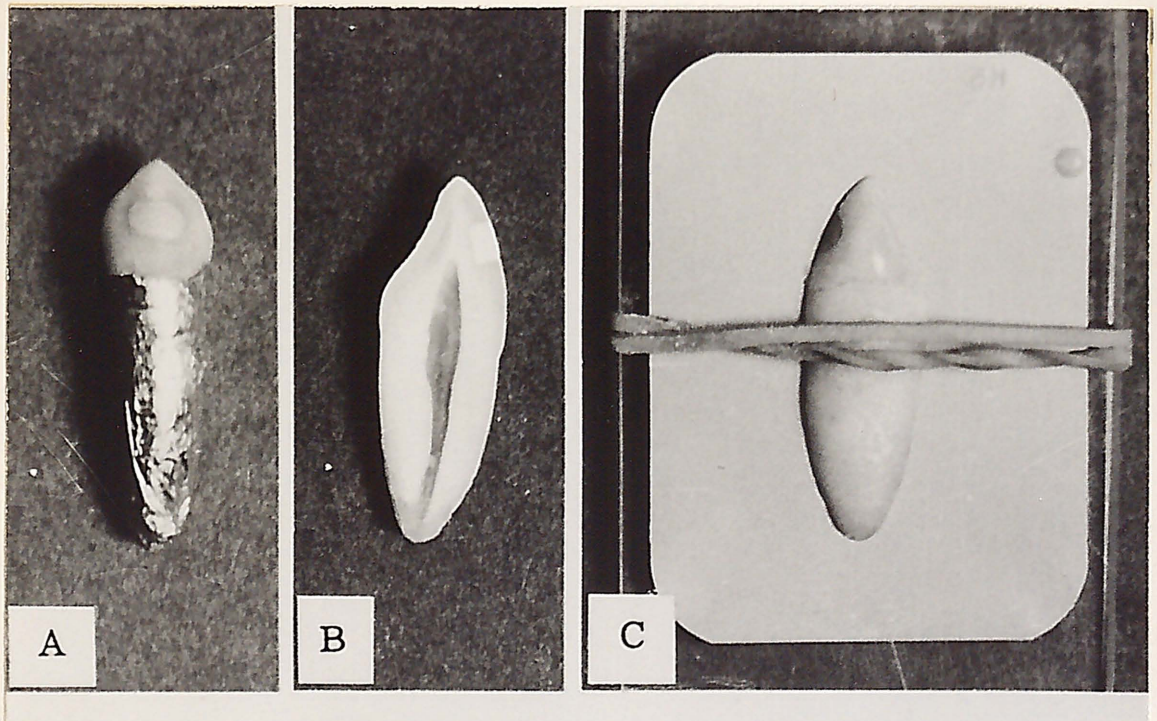

5
10
15
20
25
30
35
40
45
50
55
MINUTES
FUSE
ON
OFF

Figure 6. Preparation of tooth for isotope test and autoradiographs.

A. Tooth sealed with tin foil for immersion in isotope.

B. Tooth sectioned through restoration for placement on film.

C. Tooth mounted on film.



Sealed Sectioned On Film

Figure 7. Summary of 24-hour data on the adhesion of unfilled and composite resins. Sevriton with acid etch (values obtained from Lee's Study[72]), Sevriton with acid etch (Group I), Adaptic with acid etch (Group II), Adaptic without etch (Group III), HL-72 with acid etch (Group IV), HL-72 without etch (Group V).

24 HRS. ADHESION

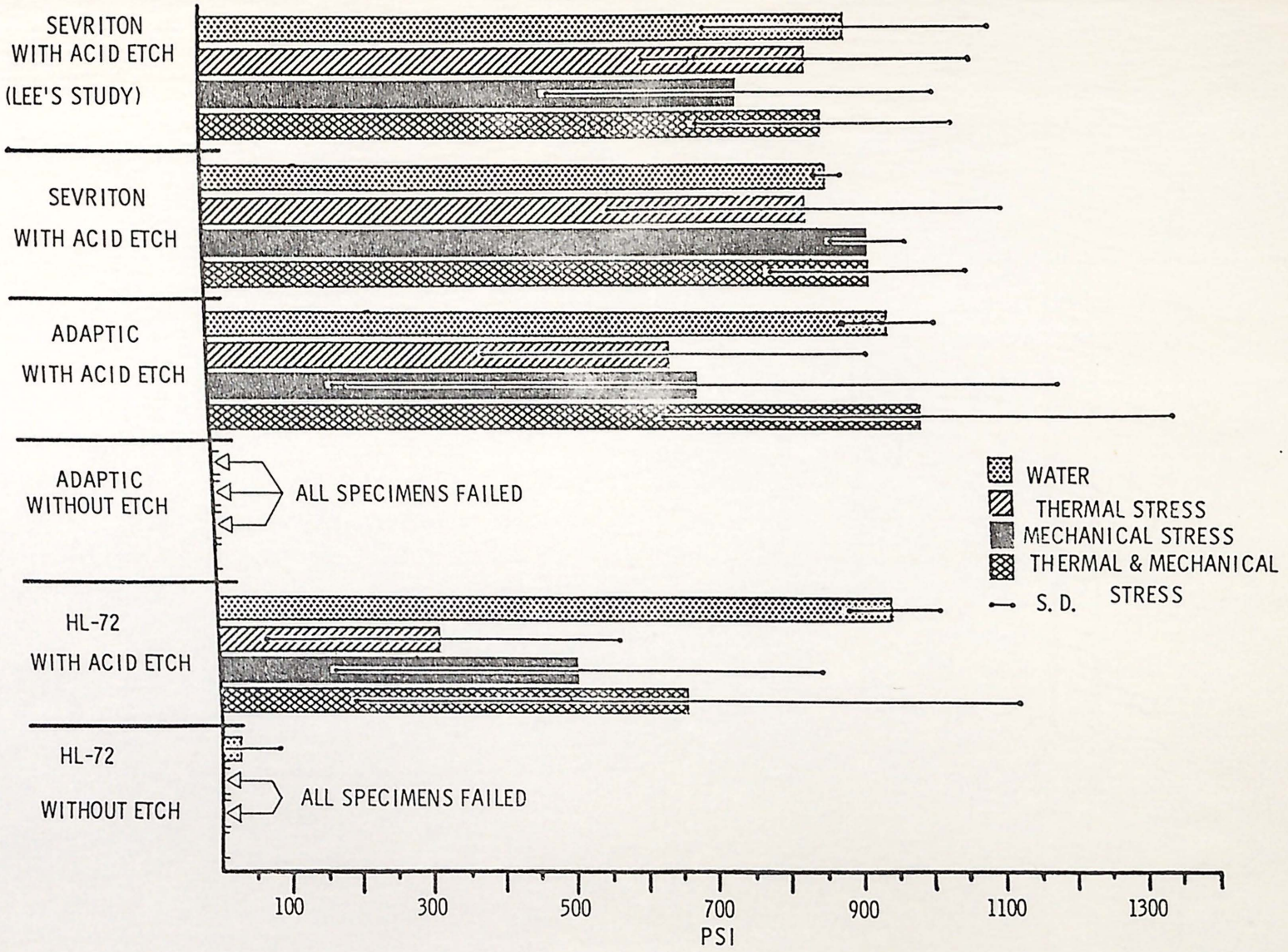


Figure 8. Summary of 30-day data on the adhesion of unfilled and composite resins. Sevriton with acid etch (values obtained from Lee's study[72]), Adaptic with acid etch (Group II), Adaptic without etch (Group III), HL-72 with acid etch (Group IV), HL-72 without etch (Group V).

30 DAYS ADHESION

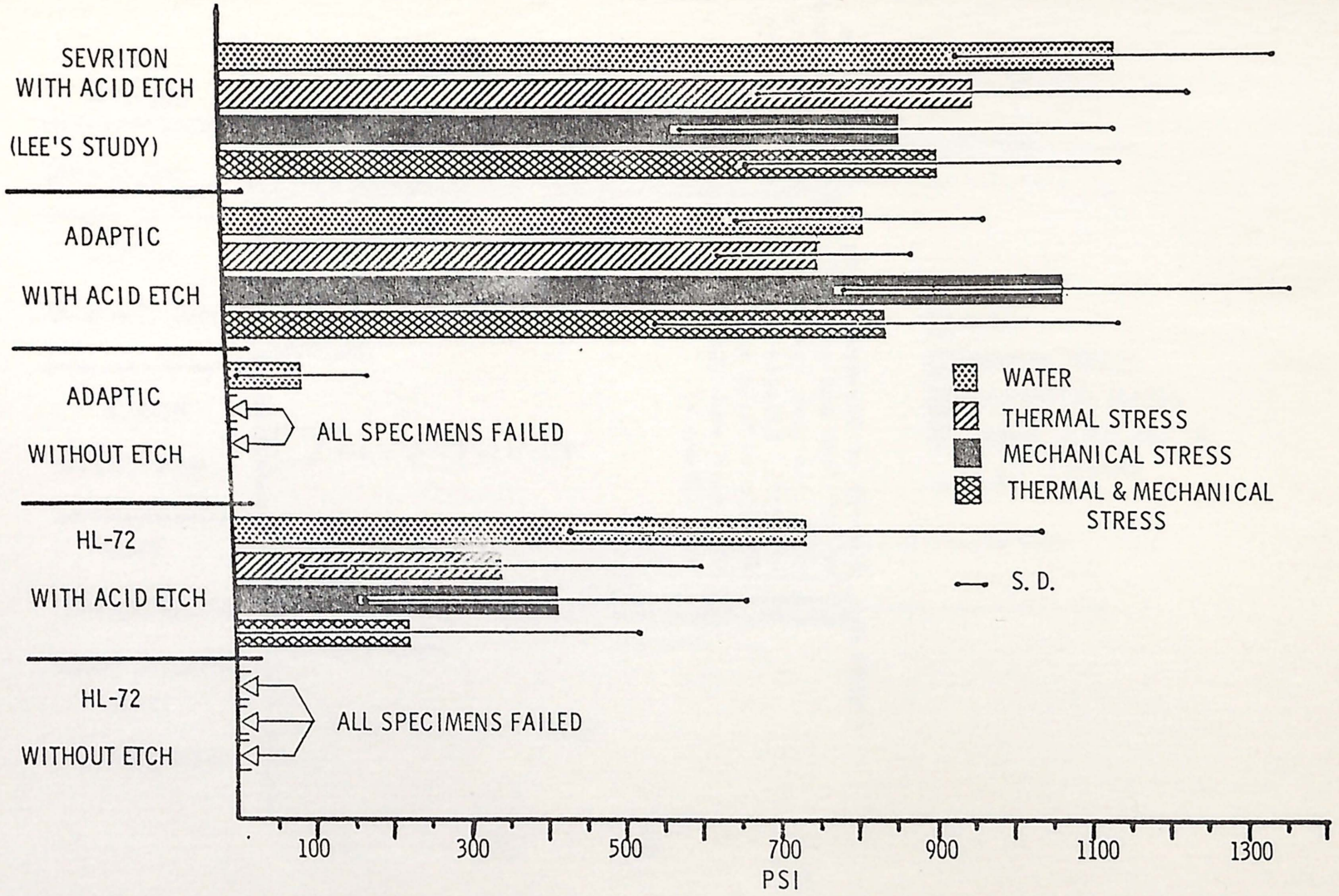


Figure 9. Summary of six-month data on the adhesion of unfilled and composite resins. Sevriton with acid etch (values obtained from Lee's study[72]), Adaptic with acid etch (Group II), Adaptic without etch (Group III), HL-72 with acid etch (Group IV), HL-72 without etch (Group V).

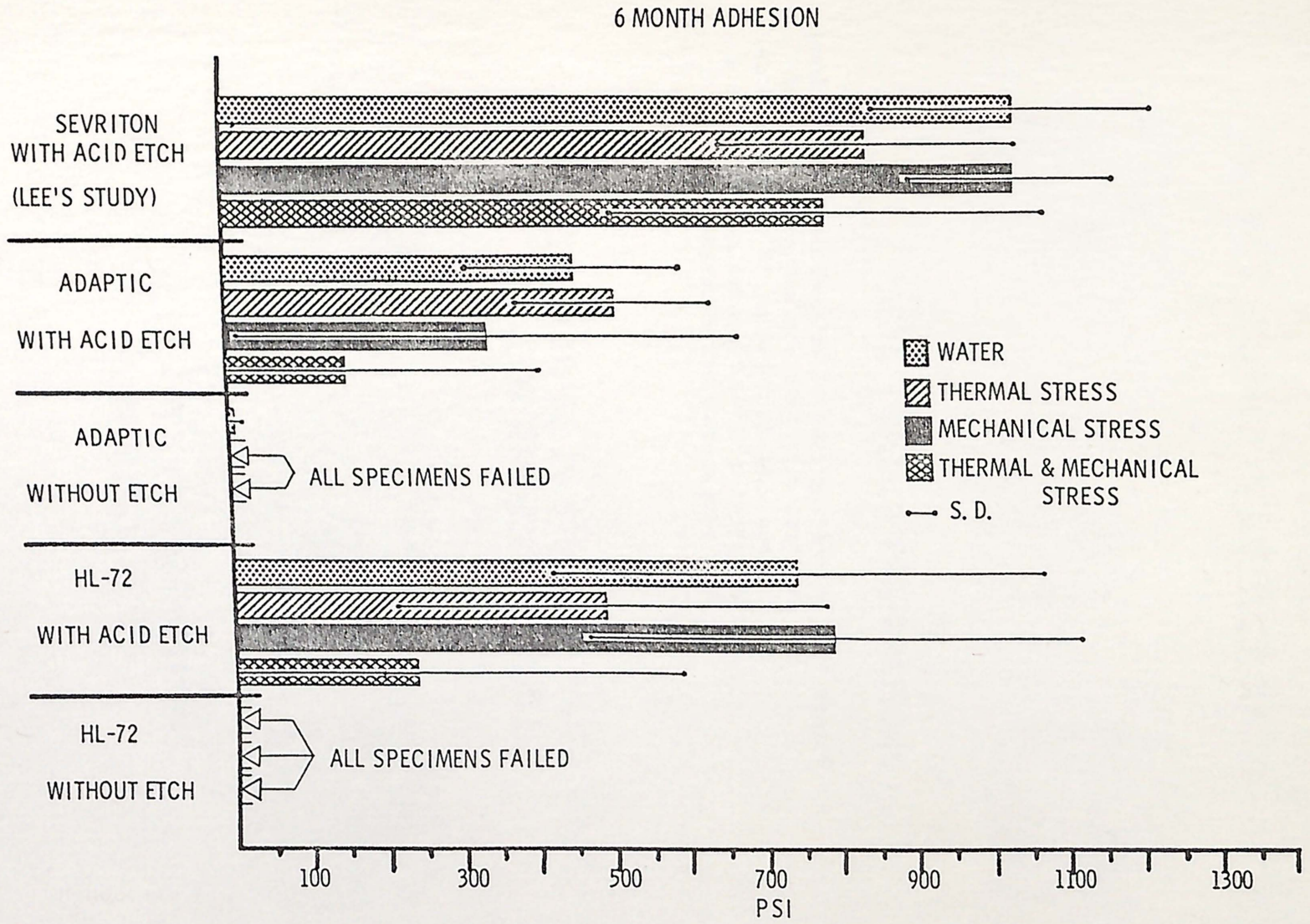

6 MONTH ADHESION
SEVRITON WITH ACID ETCH (LEE'S STUDY)
ADAPTIC WITH ACID ETCH
ADAPTIC WITHOUT ETCH
ALL SPECIMENS FAILED
HL-72 WITH ACID ETCH
HL-72 WITHOUT ETCH
ALL SPECIMENS FAILED
WATER
THERMAL STRESS
MECHANICAL STRESS
THERMAL & MECHANICAL STRESS
S. D.
100
300
500
700
900
1100
1300
PSI

Figure 10. Autoradiographs of acid-etched preparations restored with Sevriton and either stored for one-week in water at 37°C or stored and subjected to 2500 temperature cycles at a 40°C temperature differential.

ONE WEEK STORAGE IN DISTILLED WATER - 37° C

ACID - ETCHED PREPARATIONS

ONE WEEK STORAGE IN DISTILLED WATER - 37° C
AND 2500 TEMPERATURE CYCLES

ACID - ETCHED PREPARATIONS
SEVRITON RESIN

Figure 11. Autoradiographs of acid-etched and non-etched preparations restored with Adaptic after one-week storage in Water at 37°C.

ONE WEEK STORAGE IN DISTILLED WATER - 37° C

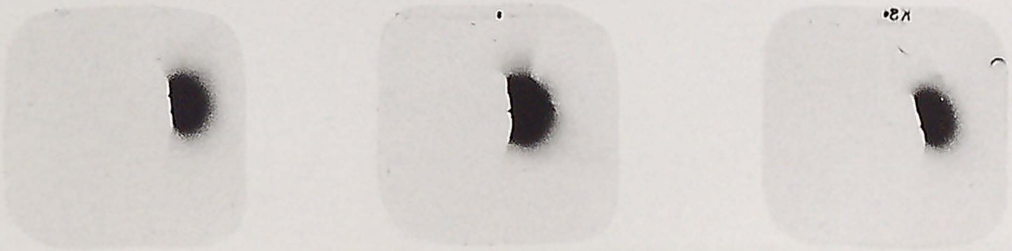
ACID - ETCHED PREPARATIONS

CONTROL PREPARATIONS
ADAPTIC

Figure 12. Autoradiographs of acid-etched and non-etched preparations restored with HL-72 after one-week storage in water at 37°C.

ONE WEEK STORAGE IN DISTILLED WATER - 37° C

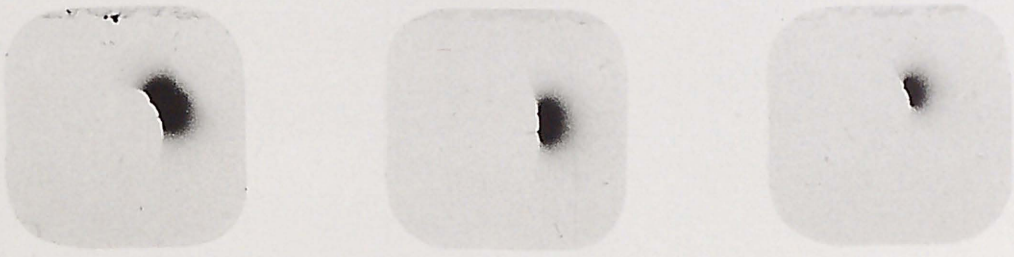
ACID - ETCHED PREPARATIONS



CONTROL PREPARATIONS
HL - 72

Figure 13. Autoradiographs of acid-etched and non-etched preparations restored with Adaptic and stored for one week in water at 37°C and subjected to 2500 temperature cycles at a differential of 40°C.

ONE WEEK STORAGE IN DISTILLED WATER - 37° C
AND 2500 TEMPERATURE CYCLES



ACID - ETCHED PREPARATIONS

CONTROL PREPARATIONS
ADAPTIC

Figure 14. Autoradiographs of acid-etched and non-etched preparations restored with HL-72 and stored for one week in water at 37°C and subjected to 2500 temperature cycles at a 40°C temperature differential.

ONE WEEK STORAGE IN DISTILLED WATER - 37° C
AND 2500 TEMPERATURE CYCLES

ACID - ETCHED PREPARATIONS

CONTROL PREPARATIONS
HL - 72

DISCUSSION

PART I:

ADHESION OF COMPOSITE AND UNFILLED RESINS

The purpose of the study was to determine if etching the enamel surface with 50 per cent phosphoric acid would increase the bond strength of composite resins to enamel in the same manner that it increases the bonding of unfilled resins to enamel. The results indicated that the retention of the composite resins, Adaptic and HL-72, on bovine enamel was appreciably increased when the enamel was etched with 50 per cent phosphoric acid.

These results support the recent observations of Sharpe and Grenoble[99] who observed resin tag formation when composite resins were applied to acid etched enamel. Their work indicates that these resin tags were similar to those observed on unfilled resins, and it was thought that these tags would increase retention. In another investigation by Brauer and Termini[101] different types of acids were employed as enamel pretreating agents. They observed increased adhesion of composites when placed on etched enamel.

The following observations can be made from comparing Figures 7,8, and 9 and reviewing Tables X,XI,XII,XIII. (1) Very few of the unetched specimens had any retention and acid etching the enamel greatly improved the retention. (2) The Adaptic composite resin and the unfilled resin (Sevriton) have no significant differences in their initial bond strengths to etched enamel surfaces. (3) As the storage time was increased, the bond strengths of the unfilled resin (Sevriton) and the composite HL-72 to etched enamel were statistically unaffected

but the Adaptic composite resins developed a significant loss in retention. (4) When the HL-72 resin specimens were compared to Adaptic resins, there were no significant differences in initial bond strengths, but the HL-72 specimens were less affected by storage time.

The increase in retention that occurred when the enamel surface was etched was probably due to several factors: (1) Surface contaminants may have been removed, thus increasing wettability. (2) removal of the prism core of the treated enamel may have increased mechanical retention, and (3) a larger surface area which was more reactive was probably created.

Photomicrographs have shown that the enamel prism cores are dissolved away by pretreating the enamel with acid. The result is a "honey-combed" surface with microscopic pores. It has been postulated that the occurrence of "resin tags" formed at the interface of the acid etched enamel surface and the resin is the result of the resin's penetration into these microscopic pores.

Visual examination of each specimen revealed that the majority of the unfilled resin specimens fractured partially (adhesive-cohesive) in the material whereas the composites separated at the tooth resin interface. This indicates that the bond strength of the unfilled resins to acid-etched enamel exceeds the tensile strength of the resin, whereas the composite resin bond strength was less than the tensile strength of the material.

The different values observed for the unfilled resin specimens and the composite resin specimens with increased storage time may be

the result of the different properties of the resins. The composite resins were more viscous than the unfilled resins and thus may not have wet the enamel surface as well as the unfilled resins did. Consequently voids may have been created at the interface due to the poorer wetting or perhaps due to contact of the composite filler with the enamel surface. Initially the voids may have played only a minor role in affecting the tensile bond strength. These initial effects may account for the larger standard deviation observed for the composite resins than for the unfilled resins. Inconsistencies observed in the results may also be attributed to poor wetting. For example, the 30-day specimens of HL-72 seemed to have a lower retention than the 6-month specimens which would not be anticipated. As storage time increased, surface dewetting and crack propagation may have occurred with the net effect of decreasing the bond strength. The fact that the HL-72 specimens did not develop a significant loss of bond strength with storage time may be due to its having a viscosity somewhere between Adaptic and Sevriton.

PART II

MARGINAL LEAKAGE

Improvement in the marginal seal of an unfilled resin (Sevriton) after one-week storage in water when the cavity preparation was etched with a 50 per cent solution of phosphoric acid for sixty seconds has been observed by Lee.[72] This same degree of improvement is also evident for composite resins (Adaptic and HL-72) when compared to restorations placed in etched and non-etched preparations and stored for one

week in distilled water. Pretreating the tooth's surface with acid probably improves the retentiveness of the restoration by some or all of the mechanisms discussed earlier in this paper.

The marginal leakage of unfilled resin (Sevriton) restorations after they were subjected to 2500 thermal stress cycles was increased. The leakage patterns of these restorations were similar to those described by Lee[72] for this material. When composite resins (Adaptic and HL-72) were subjected to the same treatment, the leakage patterns were almost identical to those of the unfilled resin restoration.

Although the composite resins as a group have a lower coefficient of thermal expansion than the unfilled resins, the difference was not demonstrated by these data. It is possible that the slightest difference in the coefficient of thermal expansion of tooth structure and resin materials is sufficient to produce surface dewetting and hence this marginal leakage.

With reference to the relative ease of manipulation of composite and unfilled resins, it is the author's opinion that it was more difficult, at least for him, to develop a standard method of placement for the composite resins. More practice was needed to develop a technic whereby consistent results were attained with the composite resins, whereas the unfilled resin consistently gave reproducible results from the first. The higher viscosity of the composite resin and its tendency to entrap air, thus producing voids, were felt to be at least partially responsible for some of the problems in perfecting the procedures of insertion of the composite resins.

SUMMARY AND CONCLUSIONS

The purpose of this laboratory study was to determine whether the bond strength of composite resins and unfilled resins are affected similarly when applied to enamel surfaces which had been previously etched with 50 per cent phosphoric acid. A tensile test was used to measure the bond strength of the resins to the tooth surface.

A total of 552 samples were placed into five principal groups. In Group I Sevriton was placed on acid etched enamel; in Group II Adaptic was placed on acid etched enamel; in Group III Adaptic was placed on unetched enamel; in Group IV HL-72 was placed on acid etched enamel; in Group V HL-72 was placed on unetched enamel. The five groups were subjected to storage in water for 24 hours, 30 days and 6 months. The effects of temperature cycling and intermittent tensile stress cycling on the strength of the bond also were observed.

The following conclusions were made: (1) pretreating the enamel surface with 50 per cent phosphoric acid for 60 seconds significantly increased the bond strength of composite resins; (2) when placed on acid etched enamel, there was no statistically different initial bond strength for the Adaptic composite resins and unfilled Sevriton resins; (3) with prolonged water storage, the Adaptic composite resins developed a significant loss of bond strength when compared to the unfilled Sevriton resins, (4) when compared to Adaptic resins, the HL-72 resin specimens were not significantly different in initial bond strengths. However, the HL-72 specimens were statistically less affected by storage time.

Adaptic, HL-72, and Sevriton resins were placed in 120 class V restorations. Sixty of the restorations were etched with 50 percent phosphoric acid; the remainder of the restorations were left unetched. One-half of the acid etched and non-etched specimens were thermal cycled 2500 times over a period of one week. The remainder of the etched and non-etched preparations served as controls and were stored one week in water.

Under the conditions of this study, the following conclusions were drawn: (1) Acid etching enhances the marginal seal of both composite and unfilled resins, (2) both composite and unfilled resins experienced increased marginal leakage in acid etched preparations when thermal cycled; and (3) there were no observable differences in the marginal seal of unfilled resins and composite resins when placed in acid etched cavity preparations.

REFERENCES

1. Semat, Henry: Fundamentals of Physics. Rinehart & Co., 1951, p. 218.

2. Newman, George: Plastic Orthodontic Attachments to Tooth Enamel. J New Jersey Dental Society, 35:346, 1964.

3. Phillips, R. W.: Certain biological considerations in the use of restorative materials. New York State Dent J, 28:397, 1962.

4. Phillips, R. W.: Advances in adhesive restorative dental materials. J Dent Res, 45:1662, 1966.

5. Lee, H. and Neville, Kris: Handbook of Biomedical Plastics, Pasadena Tech Press, 1971.

6. Zisman, W. A.: Liquid displacement from solid surfaces. In second workshop, Adhesive Restorative Dental Materials. Ph. Publication No. 1494, 1965, pp. 21-40

7. Provenza, D. U., Sardawa, R. C.: Optical and ultrastructure studies of enamel and dentin surfaces as related to cavity preparation. In second workshop, Adhesive Restorative Dental Materials, Ph. Publication No. 1494, 1965, p. 68.

8. Mahler, D. B., Terkla, L. G.: Analysis of stress in dental structures. Dent Cl N Amer, Nov., 1958, p. 789.

9. Eirich, F. R.: Reinforcement of polymers. J Dent Res 46:1193, 1967.

10. Massler, M.: Discussion. In first workshop, Adhesion restorative materials, National Institute of Health, 1961, p. 65.

11. Phillips, R. W.: Preface. In second workshop, Adhesives Restorative Dental Materials. Ph. Publication No. 1494, 1965.

12. Brauer, G. M.: Measurement of the surface area and the heats of wetting of dentin powders. In second workship, Adhesive Restorative Dental Materials, Ph. Publication No. 1494, 1965, p. 203.

13. Schartz, A. N., and Galligan, J. D.: Tooth conditioning agents for providing adhesion of restorative materials. In second workshop, Adhesive Restorative Dental Materials, Ph. Publication No. 1494, 1965, p. 132.

14. Patrick, R. L.: and Kaplan, C. M.: Rubbery polymers as intermediate layers between tooth structure and restorative materials. In second workshop, Adhesive Restorative Dental Materials, Ph. Publication No. 1494, 1965.

15. Kirn, J. R., and Leidleiser, H., Jr.: Report on efforts to grow large single crystals of Hydroxy-apatite. In second workshop, Adhesive Restorative Dental Materials, Ph. Publication No. 1494, 1965, p. 41.

16. Hess, W. C.: Organic components of enamel and dentin. In first workshop, Adhesive Restorative, Material Institutes of Health, 1961, p. 10.

17. Posner, Aaron S.: The structure of the mineral portion of teeth, In first workshop, Adhesive Restorative, Material Institute of Health, 1961, p. 15.

18. Lee, H. K.; Cupples, A. L., and Swartz, M. L.: Epoxy Resin Dental Materials. Research Report 68-140. The epoxylite Corporation, S. El. Monte, Calif., 1968, pp. 62-80.

19. Munia, F.; Nakagaiua, K., and Masuhaea, E.: New Direct Bonding System for Plastic Brackets. Amer J Ortho, 59:350-61, April, 1971.

20. Lee, H.: Advances in the synthesis of epoxy resins for adhesion to dry and wet tooth structure. In second workshop, Adhesive Restorative Dental Materials, Ph. Publication No. 1494, 1965, p. 232.

21. Scouboe, P. J.; Paffenbarger, G. C., and Sweeney, W. T.: Resin cements and posterior type direct-filling resins. J Amer Dent Assoc 52:584, 1956.

22. Bowen R. L.: Adhesive bonding of various materials to hard tooth tissues. II: Bonding to dentin promoted by a surface-active comonomer. J Dent Res 44:895, 1965.

23. Berskin, L.: Methods and factors involved in bonding orthodontic attachments to enamel. J Nihon Univ Sch Dent. 7:96, 1965.

24. Swanson, L. T., and Beck, J. F.: Factors affecting bonding to human enamel with special reference to a plastic adhesive. J Amer Dent Assoc 61:581, 1960.

25. Matsui, A. and Minogughi, G.: Experimental study about the adhesion to the tooth surface. J Dent Res 42:754, 1963.

26. Patrick, R. L.; Kaplan, C. M., and Beaver, D. R.: Improved dental restorative systems. J Dent Res 47:12, 1968.

27. Chang, R., and Uy, K. C.: An approach to the study of the mechanism of adhesion to teeth. In second workshop, Adhesive Restorative Dental Materials, Ph. Publication No. 1494, 1965, p. 103.

28. Newman, G. V., and Sharpe, L. H.: On the wetability of tooth surfaces; Preliminary investigation. J New Jersey Dent Soc 37:289, 1966.

29. Phillips, R. W.; Swartz, Marjorie L., and Norman, R. D.: Materials for the Practicing Dentists. St. Louis, C.V. Mosby Co., 1969.

30. Phillips, R. W.: Some common causes for failure of materials in operative dentistry. J. N. Carolina Dent Soc 38:241, 1955.

31. Phillips, R. W.: Some common causes for failure of materials in operative dentistry. J Indiana Dent Ass 34:9-14, 1955.

32. Seltzer, Samuel: The penetration of microorganisms between the tooth and direct filling resin. J Amer Dent Ass 51:560, 1955.

33. Sansen, R. E.; Armstrong, W. E., and Simon, W. I.: Penetration of radio calcium through acrylic margins. J Dent Res 31:485, 1952. (Abstract)

34. Masuhat E. E.; Tarumi, N., and Nakabayashi, N.: Studies on dental self-curing resins: comparison with some alkylborons as initiators for self-curing resins. Dent Inst Tokyo Med and Dent Univ 2:622, 1965.

35. Bowen, R. L.: Development of an adhesive restorative material. In second workshop, Adhesive Restorative Dental Materials, Ph. Publication No. 1494, 1965, p. 225.

36. Khowassah, M. A. F., and Sahs, E. A.: The sealing properties of methyl-2-cyanocrylate as an adhesive in dentistry. J Dent Res 45:376, 1966.

37. Blair, G. A. S.: Adhesives. Dent Pract 17:359, 1967.

38. Buonocore, M. G., and Casciani, C. A.: Synthesis and properties of certain urethanis for potential use in restorative dentistry. New York State Dent J 35:135, 1969.

39. Lee, H. K., and Swartz, M. L.,: Sealing of developmental pits and fissures. Part I an in vitro study. IADR PROGRAM OF ABSTRACTS AND PAPERS, 1970, p. 149.

40. Carderelli, N. F.: Barnacle cement as a dental restorative adhesive. Bethesda, Maryland, National Institute of Dental Research, National Institute of Health, 1968.

41. Harrison, G., and Philpott, D. E.: Bioadhesives in invertebrate phyla. In second workshop, Adhesive Restorative Dental Materials, Ph. Publication No. 1494, 1965, p. 188.

42. Eirich, F. R.: Reinforcement of polymers. J Dent Res 46:1193, 1967.

43. Bowen, R. L.: A new restorative material. J Dent Res 34:738, 1955. (Abstract)

44. Bowen, R. L.: Synthesis of a silica resin direct filling material: Progress report. J Dent Res 37:90, 1958. (Abstract)

45. Bowen, R. L.: Properties of a silica-reinforced polymer for dental restorations. J Amer Dent Assoc 66:57, 1963.

46. Bowen, R. L., and Argentar, H.: Dimethacrylate monomers for preparing composite restorative materials. IADR ABSTRACTS, 45th General Meeting, 1967, p. 175.

47. Bowen, R. L.: Effect of particle shape and size distribution in a reinforced polymer. J. Amer Dent Assoc 69:481, 1964.

48. Chang, R. W.; Dahlman, K. E., and Rueb, J. T.: Properties of a glass reinforced polymeric material for dental filling. IADR ABSTRACTS, 43rd General Meeting, 1965, p. 82.

49. Swartz, M. L.: Personal Communication.

50. Bowen, R. L., and Rodriguez, M. M.: Tensile strength, testing method, and values for some dental materials. J Dent Res 39:768, 1960. (Abstract)

51. Bowen, R. L., and Rodriguez, M. S.: Tensile strength and modulus of elasticity of tooth structure and several restorative materials. J Amer Dent Assoc 64:378, 1962.

52. Hollenback, G. M.; Villanyi, A. A., and Shell, J. S.: A Report on the physical properties of a new restorative material (addent). J S Calif Dent Assoc 34:250, 1966.

53. Buonocore, M. G.; Matsui, A. K., and Yamaki, Masas: Abrasion of restorative materials. New York Dent J 32:395, 1966.

54. Peterson, E. A. II; Phillips, R. W., and Swartz, Marjorie L.: A comparison of the physical properties of four restorative resins. J Amer Dent Assoc 73:1324, 1966.

55. Custer, Frederic: Physical properties of four filling resins. Part I J D C Dent Soc 44:15, 1969.

56. Buonocore, M. G.: New anterior restorative materials. Int Dent J 18:406, 1968.

57. Macchi, R. L., and Craig, R. G.: Physical and mechanical properties of composite restorative materials. J Amer Dent Assoc 78:328, 1969.

58. Guzman, H. G.; Swartz, M. L., and Phillips, R. W.: Marginal leakage of dental restorations subjected to thermal stress. J Prosth Dent 21:166, 1969.

59. Ryge, G.: Clinical evaluation of adhesive restorative materials. In second workshop, Adhesive Restorative Dental Materials, Ph. Publication No. 1494, 1965, p. 258.

60. Avery, David R.: A composite resin versus an amalgam: A study of certain properties and the design and initiation of a clinical investigation. Thesis. Indiana University School of Dentistry, 1971.

61. Schulman, J.: A clinical evaluation study of the 3M brand addent dental restorative system. IADR ABSTRACTS, 43rd General Meeting, 1965, p. 82.

62. Johnson, B. E.; McCure, P. J.; Cvar, J. E., and Ryge, G.: A clinical comparison of three anterior restorative materials. IADR ABSTRACTS, 45th General Meeting, 1967, p. 175.

63. Bowen, R. L.; Paffenbarger, G. C., and Mallimank, A. L.: A laboratory and clinical comparison of silicate cements and a direct-filling resin: A progress report. J Pros Dent 20:426, 1968.

64. McCure, R. J.; Cvar, J. F., and Ryge, G.: Clinical comparison of anterior and posterior restorative materials. IADR ABSTRACTS, 47th General Meeting, 1969, p. 161.

65. Laswell, H. R.; Welk, D. A., and Regenos, J. W.: Attachments of resin restorations to acid pretreated enamel. Amer Dent Assoc J 82:558-563, March, 1971.

66. Buonocore, M. G.: A simple method of increasing the adhesion of acrylic filling materials to enamel surfaces. J Dent Res 34:849, 1955.

67. Kopel, H. M.: Pretreating enamel to increase adhesion of plastic restorative materials--the etch technique. S Calif Dent Assoc J 39:752-755, 1971.

68. Newman, G. V.: Adhesion of orthodontic plastic attachments directly to teeth. J Pract Orthodont 3:339, 1969.

69. Swanson, L. T., and Beck, J. F.: Factors affecting bonding to human enamel with special reference to a plastic adhesive. J Amer Dent Assoc 61:581, 1960.

70. Bowen, R. L.: Bonding to dentin improved by pretreatment and use of surface active comonomer III. J Dent Res 44:903, 1965.

71. Muholland, R. D., and DeShazer, D. O.: The effect of acidic pretreatment solutions of direct bonding of orthodontic brackets to enamel. Angle Orthodont 38:236, 1968.

72. Lee, Brian David; Phillips, R.W., and Swartz, M. L.: A laboratory study of the adhesion of a restorative acrylic resin and a polycarboxylate cement on bovine enamel etched with fifty percent phosphoric acid, Thesis. Indiana University, 1970.

73. Buonocore, M. G.: Adhesive sealing of pits and fissures for caries prevention, with use of ultraviolet light. J Amer Dent Assoc 80:324, 1970.

74. Doyle, W. A.: Operative Dentistry In Goldman, H. M., Forrest, S. P., Byrd, D. L., and McDonald, R. E.: Current Therapy in Dentistry, 3rd ed., St. Louis, C. V. Mosby Co., 1968.

75. Law, D. B.: Prevention and treatment of traumatized anterior teeth. Dent Clin W Amer p. 615, 1961.

76. Heslin, P. L., Mechan, T. G.; Allen, F. J., and O'Sullivan, C. A.: The fractured incisor. J Irish Dent Assoc Sup 1968, pp. 1-59.

77. Ellis, R. G., and Davey, K. W.: The classification and treatment of injuries to the teeth of children. Year Book Medical Publisher, Inc., Chicago, fifth ed., pp. 13-90.

78. Lewis, T. E.: Incidence of fractured anterior teeth as related to their protrusion. Angle Orthodont 29:128, 1958.

79. Grundy, J. R.: Incidence of fractured incisors. Brit Dent J 106:312, 1959.

80. Kramer, L. R.: Accidents occurring in high school athletics with special reference to dental injuries. J Amer Dent Assoc 28:1351, 1941.

81. Hallet, G. E. M.: Problems of common interest to the pedodontist and orthodontist with special reference to traumatized incisor cases. Euto Ortho Soc 266, 1953.

82. Hardwick, S. L., and Newman, P. A.: Some observations on the incidence and emergency treatment of fractured permanent anterior teeth of children. J Dent Res 33:730, 1954 (Abstract)

83. Eichenbaum, I. W.: Correlation of traumatized anterior teeth to occlusion. J Dent Child 30:229, 4th Qtr., 1963.

84. Ayers, A. J.: Retention of resin restorations by means of enamel etching and by pins. Thesis, Indiana University School of Dentistry, 1971.

85. Albert, Monus, and Grenoble, Dale: An *in vivo* study of enamel remineralization after acid etching. Southern Calif Dent Assoc J 39:747-755, September, 1971.

86. Newman, G. V., and Facq, J. M.: The effects of adhesive systems on tooth surfaces. Amer J Ortho 59:67-75, January, 1971.

87. Koulourides, T.; Feagin, F., and Pigman, W.: Remineralization of dental enamel by saliva. AWN N Y Acad Sci 131:751-757, 1965.

88. Johnson, B.: Remineralization of slightly etched enamel. J Dent Res 44:64.

89. Lenz, H., and Muhlemann, N. R.: Repair of etched enamel exposed to the oral environment. Helv Odont Acta 7:47, 1963.

90. Nelson, R. J.; Wolcott, R. B., and Paffenbarger, G. C.: Fluid exchange at the margins of dental restorations. J Amer Dent Assoc 44:288, 1952.

91. Swartz, Marjorie L.: *In vitro* studies on marginal leakage of restorative materials as assessed by Ca^{45}. Thesis. Indiana University School of Dentistry, 1959.

92. Swartz, M. L., and Phillips, R. W.: In vitro studies on the marginal leakage of restorative materials. J Amer Dent Assoc 62:141, 1961.

93. Christen, Arden, and Mitchell, D. F.: A fluorescent dye method for demonstrating leakage around dental restorations. J Dent Res 45:1485, 1966.

94. Tani, Y., and Buonocore, M. G.: Study of marginal leakage of dye penetration into resin restorative materials. IADR 46:95, 1968.

95. Going, R. E., and Sawinski, V. J.: Microleakage of a new restorative material. J Amer Dent 73:107, 1966.

96. Going, R. E., and Loiselle, R. J.: Microleakage of a new restorative material. IADR ABSTRACTS, 43rd General Meeting, 1965, p. 82.

97. Going, R. E.; Myers, H.M., and Prussin, S. G.: Quantitative method for studying microleakage in vivo and in vitro. J Dent Res 47:1128, 1968.

98. Lee, H. L., and Swartz, M. L.: Scanning electron microscope study of composite restorative materials. J Dent Res 49:149, 1970.

99. Sharpe, E. C., and Grenoble, D. E.: Dental resin penetration with acid etched subsurface enamel. S Calif Dent Assoc J 39:741-746, September, 1971.

100. Gwinnett, G. M., and Termini, D. J.: A study of enamel adhesives. Arch Oral Biol 12:1615, 1967.

101. Brauer, G. M., and Termini, D. J.: Bonding of bovine enamel to restorative resin: Effect of pretreatment of enamel. J Dent Res 51:151, January-February, 1972.

102. Hanke, Gilberto: Screening test methods and their application in measuring adhesion of selected dental resins. Thesis. Indiana University School of Dentistry, 1968.

CURRICULUM VITAE

Robert Wayne Aubuchon

August 25, 1946	Born to Howard and Agatha Aubuchon, Oakland, California
1964-1967	American River College
June 12, 1971	D.D.S., University of California School of Dentistry, San Francisco, California
1971-1973	Graduate Student, Indiana University at Indianapolis, Indiana, School of Dentistry
July 29, 1972	Married Virginia Elizabeth Milestone, San Francisco, California

Professional Organizations

American Dental Association

American Society of Dentistry for Children

ABSTRACT

A LABORATORY COMPARISON OF THE ADHESION OF UNFILLED AND COMPOSITE RESINS TO ACID ETCHED ENAMEL

ROBERT W. AUBUCHON D.D.S.
INDIANA UNIVERSITY SCHOOL OF DENTISTRY
INDIANAPOLIS, INDIANA

The purpose of this laboratory study was to determine if the bond strengths of composite resins and unfilled resins was affected similarly when applied to enamel surfaces which had been previously etched with 50 per cent phosphoric acid. The test specimens were subjected to 24 hours, 30 days, and 6 months storage in water and then subjected to temperature stress cycling and intermittent tensile stress cycling. A tensile test was used to measure the bond strengths of the composite resins (Adaptic and HL-72) and the unfilled resin (Sevriton).

The following results were obtained: (1) Pretreating the enamel surface with 50 per cent phosphoric acid for 60 seconds significantly increased the bond strength of composite resins; (2) when placed on acid etched enamel, there was no significant difference in initial bond strengths obtained for the Adaptic and unfilled Sevriton resins; (3) with prolonged water storage, the Adaptic composite resins developed significant loss of bond strength when compared to the unfilled Sevriton resins and the composite HL-72 resins; (4) when Adaptic resins and the HL-72 resin specimens were compared, there was no significant difference in initial bond strengths but the HL-72 specimens were less affected by storage time.

Ca^{45} was used to assess the marginal seal of Adaptic, HL-72, and Sevriton in acid etched and non-etched Class V restorations.

One-half of the specimens were thermal cycled 2500 times and stored in water for one week. Control specimens were tested at the end of one week without the thermal cycle.

On the basis of these results, it was concluded that acid etching enhances the marginal seal of both composite and unfilled resins. Both composite and unfilled resins experienced increased marginal leakage when the acid etch preparations were thermal cycled, but there were no observable difference in the marginal seal of unfilled resins and composite resins when placed in acid etched restorations.